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PHOTO-PROCESSES IN GASEOUS AND LIQUID SYSTEMS

BY

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AND

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LECTURERS IN PHYSICAL CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL

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PREFACE.

The slow development of Photochemistry compared with other branches of Physical Chemistry is possibly due to two main causes. On the one hand, the experimental study of photochemical reactions involves in general a somewhat difficult technique if quantitative data of the highest value are required; on the other hand, the development of the theoretical side of the subject had to await the remarkable advances made in Physics in the last two or three decades. The introduction of the quantum theory by Planck and its application to Photochemistry by Einstein, together with the inception and rapid achievements of Bohr's theories of atomic constitution and the origin of spectral lines, have, however, supplied the necessary background for the evolution of this branch of Chemistry, and have stimulated a new interest in the subject, with the result that its problems are now being intensively re-investigated. In writing this book, one of our objects was to present an account of Theoretical Photochemistry in which the results of these recent investigations would be incorporated; it was realised, however, that if, as it is hoped, the work might serve as a textbook on the subject, much more subject-matter than the purely photochemical would have to be included. The foundations on which the present-day photochemist must build are those branches of modern physical theory which are concerned with the interaction of radiation and matter, and include the theory of atomic and molecular structure, atomic and molecular spectra, and photoluminescence. Actually, we have deemed it advisable to devote nearly half the space at our disposal to these topics. In addition, there is included a chapter on chemiluminescence—the inverse phenomenon to photochemical change—and its interpretation along modern physical lines. For various reasons, we have, as indicated in the title of the book, confined the discussion of photochemical reactions (and of photo-processes generally) mainly to reactions occurring in gaseous and liquid media. This eliminates the important subjects of photosynthesis of carbohydrates and the action of light on photographic plates, as well as topics of lesser importance, such as phototropy and photogalvanic action. Apart from considerations of space, it was felt that adequate treatment of these matters would require that more attention be devoted to the non-photochemical aspects of these phenomena than to the photochemical, and that comparatively little of interest from the standpoint of *Theoretical* Photochemistry has yet accrued from the study of these subjects. Our discussion of photo-reactions in the second half of the book deals to a considerable degree with the question of reaction mechanism. It is to be emphasised that at present much that is speculative has necessarily to be introduced into the hypotheses which serve in this connection, and that on many questions considerable divergence of opinion exists. While therefore in these chapters there are many examples in which judgment has perforce been suspended, doubtless in other cases we have been too dogmatic, and the reader should be prepared to find further instances in which he should exercise caution. There exists at present a rather striking contrast between the fairly generally accepted interpretations of the physical reactions of atoms and diatomic molecules with radiation and the extremely conjectural hypotheses advanced for the explanation of photochemical reactions, especially of those occurring in liquid solution. The bridging of the gap between the two has perhaps hardly yet begun, but it seems likely that it will come about by developments of the theory of molecular spectra resulting in more exact knowledge of the primary action of light on polyatomic molecules and on substances in the liquid state. Of the physical problems of major interest to the photochemist, undoubtedly one of the most important which awaits attention is that dealing with the interpretation of absorption spectra in liquid solution.

R. O. G.
A. McK.

DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF LIVERPOOL,
August, 1929.

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CHAPTER I.

INTRODUCTORY.

THE NATURE OF RADIATION.

Radiant Energy.—By radiation we mean that form of energy which can be transmitted through space without the help of any material medium or vehicle. This definition excludes from the category of radiation certain types of emission such as cathode and β-rays, which formerly, in the absence of sufficient knowledge of their true character, were classed as radiations but which we now know to involve the spatial transfer of matter or electrons. In these latter cases, the energy transferred exists as kinetic energy of an electron stream.

Recognition of the existence of any radiation depends upon its interaction with matter. Whilst a material medium is not necessary for its propagation, radiant energy must always have a material source, and it cannot be destroyed or modified in any way except by reaction with material bodies. Its production or its disappearance naturally involves a loss or gain of some other form of energy by the substance which emits or absorbs it. Infra-red radiation is detected by its transformation into energy of heat motion, visible light by its chemical action upon the visual purple in the retina of the eye, ultra-violet light and X-rays by their ionising action upon matter or by their photochemical action upon a photographic plate, etc. In addition to the capacity of matter to emit and to absorb radiant energy, however, the reaction may, under certain conditions, be limited to the purely " optical " effects of reflection, refraction, interference, and diffraction. Normally such effects as these do not involve any change in the quality of the participating radiant energy or its transformation into other forms of energy, but only modify its direction of propagation and its distribution in space. The chief experimental methods for the measurement of the quality of radiation (by the prism and the diffraction grating) are based upon well-defined variations with the nature of the radiation in such optical effects.

Radiation as a Wave Motion.—The early history of radiation was the history of visible light—the only type of radiation then recognised—and the first attempts to produce a theory of radiation laid particular stress upon the interpretation of the phenomena generally dealt with under the headings of geometrical and physical optics. The undulatory nature of the propagation through space of visible light was first developed by Huyghens (1678), but his efforts to explain various optical phenomena on this basis were to a great extent vitiated by his belief that the wave motion was longitudinal in character, analogous to the case of sound waves. Fresnel (1814) first showed that the general optical properties of visible light receive a simple and consistent explanation if the light be regarded as transmitted through space in the form of *transverse* displacement vibrations of a non-material elastic medium—the luminiferous ether. The mechanical wave theory of Fresnel relates the quality or colour of light to the periodicity of the ether vibration to which it corresponds, the intensity of the light at any point in space to the amplitude of the ether vibration at that point, and the state of polarisation to the degree of asymmetry of the ether displaced in the wave front.

The nature and manner of propagation of a transverse wave motion in an elastic medium is in the simplest case described analytically by means of an equation of the type

$$y = a \,.\, \sin 2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right) \quad . \quad . \quad . \quad . \quad (1)$$

This represents a train of plane waves travelling through the medium in the direction of the axis of x; y measures the transverse displacement in the medium at the position x and at the time t, a is the maximum value of this transverse displacement—the amplitude of the vibration. If attention be confined to a particular position x in the wave train, it is seen that the displacement of the medium at this point is transverse, linear, and simple harmonic in time, with a period of vibration equal to T. The form of the wave motion—what would correspond to an instantaneous photograph of the train of waves—is obtained by fixing t, and is seen to take the shape of a sine curve. The distance between two consecutive positions on the axis of x at which the transverse motions correspond exactly is the wave-length λ. The velocity of propagation of the wave train is given by $v = \frac{\lambda}{T} = \lambda\nu$, where ν is the frequency of the transverse vibration.

Such a wave motion as this in the ether corresponds, according to the mechanical theory of Fresnel, to monochromatic plane polarised light of frequency ν and wave-length λ. The intensity of the light at any point in the path of the wave train is determined by the square of the amplitude a of the ether vibration at that point. Besides such plane polarised monochromatic waves, however, we may also have monochromatic waves for which the transverse displacement in the wave front is not linear but is circular or elliptical. These represent circularly and elliptically polarised light respectively. Finally, radiation which is unpolarised may be regarded as the composite effect of wave trains (of the same frequency) polarised in all possible directions, or as a plane wave train in which the direction of polarisation is erratic, or (for purposes of mathematical analysis) as the superposition of two mutually perpendicular and synchronous linear vibrations of the same amplitude. Whatever be the state of polarisation of a monochromatic beam of radiation, it is always possible to describe it analytically as the resultant of two beams plane polarised in mutually perpendicular directions. The energy carried by the wave, or the intensity of the wave, is then determined by the sum of the squares of the amplitudes of these two component vibrations.

The concept of a medium for the propagation of radiation is not free from difficulties. The ether of Fresnel was of the nature of a continuous, all pervading, and perfectly elastic solid. To these attributes, however, physicists of the nineteenth century found it necessary to add other unique and rather fanciful properties, such as perfect incompressibility or even negative resistance to compression, to account for the absence of the longitudinal wave which should accompany transverse vibration in an elastic solid. Then again it was considered that the luminiferous ether should form the absolute stationary system of reference for all motion of matter. The Michelson-Morley experiment and the development of the theory of relativity have disposed of the utility of an ether medium in this last capacity. The propagation of radiation in space is still formally regarded for most purposes as a transverse wave motion—no longer mechanical but electromagnetic in character—but the nature of the medium of propagation, or indeed the necessity for such a medium, is no longer discussed.

Electromagnetic Theory. The Complete Radiation Spectrum.—An appreciation of the essential identity of the many types of radiant energy which we now recognise followed from Maxwell's derivation (1864) of the differential equations governing the transfer through space of an electromagnetic wave (a rapidly alternating electric displacement current and the accompanying magnetic displacement current), and his prediction that the velocity of propagation of such a wave should be equal to that of visible light. In 1887 Hertz first demonstrated the actual existence of these electrical waves, which he produced by the oscillatory discharge of a condenser, and he showed that they could be reflected, refracted, and focussed in accordance with the same laws as apply to visible light.

According to the electromagnetic theory of radiation as developed from the work of Maxwell and of Hertz, the difference between Hertzian waves and infra-red, visible, or ultra-violet light is one of degree only, the quality of the radiation being determined by the periodicity of the electric or of the magnetic displacement in the wave motion. Hertzian vibrations are characterised by a large period of vibration and a wave-length of the order of metres or even kilometres. At the other end of the scale are X-rays and γ-rays with exceedingly small periods ($10^{-17} - 10^{-20}$ sec.) and wave-lengths correspondingly minute ($10^{-7} - 10^{-10}$ cm.). For practical purposes the whole range of electromagnetic disturbances which we include under the general head of radiation is roughly sub-divided as follows :—

Type of Radiation.	Frequency Limits ($\sec.^{-1}$).	Wave-length Limits (cm.).
Electrical waves . . .	$10^5 - 3 \cdot 10^{11}$	$3 \cdot 10^5 - 10^{-1}$
Infra-red rays . . .	$10^{12} - 4 \cdot 10^{14}$	$3 \cdot 10^{-2} - 7{\cdot}5 \cdot 10^{-5}$
Visible light . . .	$4 \cdot 10^{14} - 7{\cdot}5 \cdot 10^{14}$	$7{\cdot}5 \cdot 10^{-5} - 4 \cdot 10^{-5}$
Ultra-violet light . .	$7{\cdot}5 \cdot 10^{14} - 6 \cdot 10^{15}$	$4 \cdot 10^{-5} - 5 \cdot 10^{-6}$
X- and γ-rays . . .	$3 \cdot 10^{17} - 10^{20}$	$10^{-7} - 3 \cdot 10^{-10}$

Certain portions of this complete radiation spectrum, notably the regions between short electrical waves and the extreme infra-red and between the extreme ultra-violet and X-rays, have not yet been completely explored. The types of radiation—visible and ultra-violet light—with which we shall be chiefly concerned in the present work are contained within the relatively narrow frequency range from $4 \cdot 10^{14}$ to $3 \cdot 10^{15}$ $\sec.^{-1}$. This range covers only a very small portion of the complete spectrum of electromagnetic disturbances.

The electromagnetic theory describes all types of radiation as being modifications in periodicity of essentially the same kind of disturbance. It further ascribes to them a common velocity of propagation *in vacuo*, namely the velocity of light which is $2{\cdot}998 \times 10^{10}$ cm./sec. The simplest electromagnetic process, representing plane polarised monochromatic radiation travelling in free space in the direction of the axis of x, is expressed mathematically by a transverse wave equation similar to (1) above, in which, however, for the mechanical displacement y of an elastic medium at the position x is substituted the intensity Y of an electric vector alternating in the wave front. A necessary accompaniment to this electric vector is a synchronously alternating magnetic vector β which also acts in the wave front but in a direction perpendicular to the electric vector. The complete disturbance at any point is therefore represented by the simple harmonic oscillations in the values of the two mutually perpendicular vectors Y and β acting in the plane at right angles to the direction of propagation. The modifications introduced by elliptically polarised, circularly polarised, and unpolarised radiations are described in exactly the same way as given under the mechanical wave theory of Fresnel.

Usually the radiation from any material source is not nearly monochromatic in character; the electromagnetic disturbance which it produces at any point in its path is not a simple harmonic vibration, but the electric and magnetic displacements in the wave front are both complex periodic functions of time. Mathematically, any such disturbance can be resolved into a Fourier series (or integral) of simple harmonic linear vibrations, each of which will possess a definite frequency, intensity, and state of polarisation. In practice, the prism or diffraction grating fulfils much the same purpose, by decomposing a compound beam of radiation into its spectrum, from which any desired strip of practically monochromatic radiation may be selected.

The purity of radiation selected from a resolved spectrum is conditioned by the closeness of the wave-length or frequency limits of the chosen strip. It is not possible, however, to obtain pure monochromatic radiation of finite intensity from a continuous spectrum, since under these circumstances a finite amount of radiant energy can only be associated with a finite frequency interval. The "spectral line" is the nearest approach to a monochromatic radiation in nature, but even if the individual atom or molecule can emit pure monochromatic radiation (see Chapter II.), broadening due to Doppler effects and to varying environmental influences on the large number of emitting units required to give a perceptible intensity of emission will always set a limit to the sharpness of the observed "line." In practice, then, when we speak of radiation of frequency ν we really mean the radiation within a restricted spectral range $\Delta\nu$, the limits of which lie more or less close on either side of the value ν.

A few words should be said here regarding the system of units adopted in speaking of the frequency and the wave-length of radiation. The periodicity of a monochromatic radiation is usually expressed either in terms of its *frequency* (units — sec.^{-1}) or of its *wave-number*, that is, the number of waves per centimetre of its rectilinear path of propagation *in vacuo* (units — cm.^{-1}). The wave-number of the radiation is simply its frequency divided by the velocity of light *in vacuo* ($2{\cdot}998 \times 10^{10}$ cm./sec.), and like the frequency is independent of the medium in which the beam of radiation happens to be examined. The one symbol ν is used both for frequency and for wave-number. Since the ratio of the two quantities is a universal constant and since their magnitudes differ so considerably, this practice need never give rise to any ambiguity of meaning. The *wave-length* λ of the radiation is its velocity of propagation in the medium divided by its frequency, and therefore depends upon the optical properties of the medium in which it is measured. Obviously the wave-length *in vacuo* is the reciprocal of the wave-number. Although wave-length limits given above have been expressed in centimetres, other subsidiary and more convenient units of length are normally employed in speaking of any radiation other than electrical waves. The unit $1\,\mu$ is the ten-thousandth part of a centimetre; $1\ \mu\mu$ is the ten-millionth part of a centimetre; and these units of length are normally adopted for the description of spectral regions in the infra-red and in the visible and ultra-violet respectively. Another standard of length is the Ångstrom unit (1 Å), which is the hundred-millionth part of a centimetre, and this is usually employed in an exact statement of the wave-lengths of visible and ultra-violet light and of X-rays.

Classical Electrodynamics.—Maxwell's theory describes the propagation of radiant energy through empty space or through any isotropic medium by a set of simple differential equations expressing the wave transmission of a periodic electromagnetic disturbance. The medium of propagation is assumed to be continuous, but its nature is no further specified than by a statement of its electrical conductivity, its dielectric constant, and its magnetic permeability. The phenomena of reflection and refraction are then accounted for in terms of discontinuities of these parameters at the bounding surfaces of different media. In order to interpret the production, dispersion, and absorption of radiation, however, it is necessary to be more explicit about the nature of the medium and in particular to make definite postulates regarding the ultimate emitting and absorbing units in matter.

In the older wave theories of Huyghens and Fresnel, the dispersion of light was explained by the assumption of mechanisms, elastically held about equilibrium positions in the dispersing medium, which could be set into forced vibration by the incident ether pulse. The dispersion formulæ of Sellmeier and Helmholtz were deduced on such a basis. Later, an analogous theory of dispersion which took account of the electromagnetic nature of the radiation field was worked out by Lorentz on the assumption that the material medium contains electrically charged particles capable of vibrating about positions of rest to which they are held by quasielastic forces of electrical origin. The vibrating electric vector of the incident radiant field induces forced oscillations of these charged particles, as a result of which secondary waves start out from them and interfere with the primary wave train. If the natural frequency of the charged particles is very different from that of the incident radiation, the net effect is a retardation of the transmitted wave front (normal dispersion). For frequencies which lie close to the natural frequency of the vibrating particles anomalous dispersion, selective reflection, and true absorption of the radiation occur.

Later, the charged particles of Lorentz were identified with ions and electrons, but essentially his treatment of the mutual interaction of radiation and matter formed the basis of what is now termed the classical electrodynamics of the nineteenth century. According to this, the Maxwell equations are considered to give an exact description of the radiation field. Whether or not a luminiferous ether is required for the propagation of the electromagnetic wave through space need not be explicitly stated. The equations themselves are independent of any such concept. The radiation field itself is produced in the following manner. An electromagnetic disturbance or wave starts out from each vibrating, electrically polar unit—an atomic or molecular system with spatial separation of unlike electrical charges—whose vibration involves a periodic fluctuation of its electrical moment. The frequency of the radiation emitted is identical with that of the oscillator itself; its phase, intensity, and state of polarisation are determined by the phase, amplitude, and manner of vibration of the oscillator. In this way an excited oscillator produces a continuous wave train of radiant energy at the expense of its own energy of vibration. If, on the other hand, an electrically polar unit is placed in a radiation field, the frequency of which approximates to the natural frequency of vibration of the polar unit, the latter will be induced to vibrate in sympathy with the electric vector of the field, and energy will be continuously absorbed from the field. The concept of such continuous energy exchanges between the individual oscillator and a radiation field of the same frequency is a fundamental principle of classical electrodynamical theory. How far this principle requires to be modified to explain the results of experience will be considered in the next Chapter.

THE PRODUCTION OF RADIATION.

Recognising that radiant energy ultimately owes its origin to the excitation of atoms and molecules, we may classify the practical methods for its production according to the manner of excitation of these intermediary material units. The various types of radiation then come under the following main heads :—

(*a*) *Temperature or Heat Radiation.*—This is emitted to a greater or less extent by every material system in virtue of its temperature alone. It arises from the conversion by collisions of the kinetic energy of unordered heat motion of the atoms or molecules into internal (electronic, vibrational, or rotational) energy. The so excited atoms or molecules can then either dissipate their acquired internal energy by subsequent collisions or lose it by the emission of radiation. The capacity for temperature emission is greatest for matter in the solid and liquid states of aggregation. Most solids and liquids begin to emit *visible* radiation in appreciable amount at temperatures above 500° or 600° C. Much higher temperatures are usually required, however, to produce a measurable temperature luminescence from gases and vapours. The gross intensity of temperature emission of any substance always increases rapidly with increasing temperature, but in general the spectral distribution is governed by very complex laws, which are more or less specific for each substance. Only in the case of the perfectly black body are the characteristics of the temperature emission dependent solely upon the temperature. This special case, which is theoretically of great importance, is further referred to in Chapter II.

(*b*) *Radiation due to Electrical Excitation.*—Under this heading are included arc and spark spectra, the various spectra produced by the passage of an electric discharge through gases and vapours under reduced pressures, X-rays, cathode-luminescence, and the emission accompanying the inverse photoelectric effect. In all these methods of producing radiation, electrical energy is utilised either to develop a very high local temperature with accompanying excitation or ionisation of atoms or molecules in the immediate vicinity, or to maintain a continuous supply of high speed ions or electrons which can induce other atoms or molecules to emission by collision.

(*c*) *Radioluminescence* is the luminescence produced in matter by exposure to the corpuscular " radiation " (high speed α- and β-rays) of a radioactive element.

(*d*) *Chemiluminescence.*—By this we mean the radiation which is emitted as an accompaniment to certain exothermic chemical reactions. The potential chemical energy of the reacting system is transformed into radiant energy. The familiar example is the glow which accompanies the slow oxidation of phosphorus. This mode of production of radiation is specially important from the point of view of the photochemist, as representing the reverse phenomenon to that of photochemical action. Recent developments in its study are dealt with in Chapter VI. The chemiluminescence accompanying the decay of certain animal and vegetable tissues is sometimes spoken of as *bioluminescence.*

(*e*) *Triboluminescence* is an emission of radiation which very often occurs upon the cleavage of crystals by percussion or grinding. The exact mechanism of triboluminescence is not yet known, but from certain observations it appears probable that the emission is always of the nature of a miniature spark discharge between the separated facets of the broken crystal. Closely akin to triboluminescence is the *crystalloluminescence* which attends the crystallisation from the melt or from saturated solution of many substances.

(*f*) *Photoluminescence.*—Whereas in the previously mentioned cases other forms of energy are converted into radiant energy, in photoluminescence we have the absorption of radiation by matter and its re-emission either as radiation of the same quality—*resonance radiation*, or as radiation of different quality—*fluorescence* or *phosphorescence.* A formal distinction is drawn between resonance and fluorescence where the re-emission is instantaneous and phosphorescence where the re-emission takes place over a more or less protracted interval of time subsequent to the primary act of absorption. Photoluminescent processes (particularly resonance radiation and fluorescence) are dealt with in detail in Chapter V.

GENERAL LAWS OF EMISSION.

The following laws and definitions are based entirely upon the principle of conservation of energy and upon the rectilinear propagation of light in a homogeneous, isotropic medium.

Emission from a Point Source.—When the source of radiant energy is of very small dimensions compared with the distance from the source at which the radiation is examined, it is then legitimate to regard it as a point source forming the apex of cones of radiation which it sends out into space. Let us consider the radiation which is emitted from such a point source O into a surrounding, non-absorbing, and isotropic space. The total emission from the source naturally has to traverse any imaginary surface which completely surrounds it, and the total emission is therefore defined as the amount of radiant energy falling in unit time upon such an enclosing surface. For purposes of describing the emission in any particular direction, this total emission is divided up into cones of radiation each of circular cross-section and each starting from the source as apex. Any such cone is defined geometrically by the direction of its axis *OP* in space and by the magnitude of its solid angle ω. The latter is a measure of the surface area which the cone cuts out on the sphere of unit radius which has the apex of the cone as centre. If *AOB* represent any such cone, then by virtue of the rectilinear propagation of the radiation in our isotropic medium, the same total energy is transmitted in unit time through every cross-section of this cone, whether this is a circular section such as *AB* or *CD* or an elliptical section such as *EF*, the normal to which is inclined at an angle to the axis of the cone.

If now the point source radiated uniformly in all directions, the energy flux through all cones of the same aperture would be the same. We should say that the *specific intensity* or *illuminating power* of the source was the same in all directions. However, this need not necessarily be the case. The illuminating power i of the source in any given direction is defined quantitatively as the amount of radiant energy flowing per second through any cross-section of an elementary cone of unit solid angle, the axis of which coincides with the given direction. In general i is a function of the angle variables which define the direction in space of the emission. If this be the direction *OP* (cf. Fig. 2), its orientation in space referred to the co-ordinate system (O, XYZ) is fixed by the angle θ which *OP* makes with *OZ* and by the angle ϕ which the plane *ZOP* makes with the plane *ZOX*. Any solid angle $d\omega$ whose axis lies in the direction *OP* is equal to $\sin\theta \, . \, d\theta \, . \, d\phi$. Writing the illuminating power in this direction as $i(\theta, \phi)$, the total emission within the angle $d\omega$ is given by

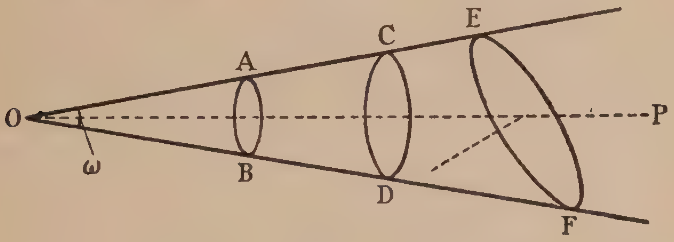

FIG. 1.

$$i(\theta, \phi)d\omega = i(\theta, \phi) \, . \sin\theta \, . \, d\theta \, . \, d\phi.$$

The total emission within any finite aperture is the integral of this taken between the assigned limits of θ and of ϕ. In particular, if $i(\theta, \phi)$ is independent of direction and equal to i, the emission within a finite cone of solid angle ω is $i\omega$, and the total emission of the source into the surrounding space $(\omega = 4\pi)$ is $4\pi i$.

If we have a surface illuminated by a point source the *intensity of illumination* at any point on the surface is the amount of energy falling in unit time upon unit area of the surface at that point. This quantity will depend not only upon the illuminating power of the source but also upon the distance of the surface element in question from the source and upon its inclination to the direction of the incident rays. Consider again an elementary cone of radiation of aperture $d\omega$ coming from the source O in the direction OP (Fig. 3). The circular cross-section AB of area $r^2 d\omega$ which is perpendicular to OP receives per second an amount of energy equal to $i d\omega$, where i is the illuminating power of O in the direction OP. The intensity of illumination of AB is therefore given by

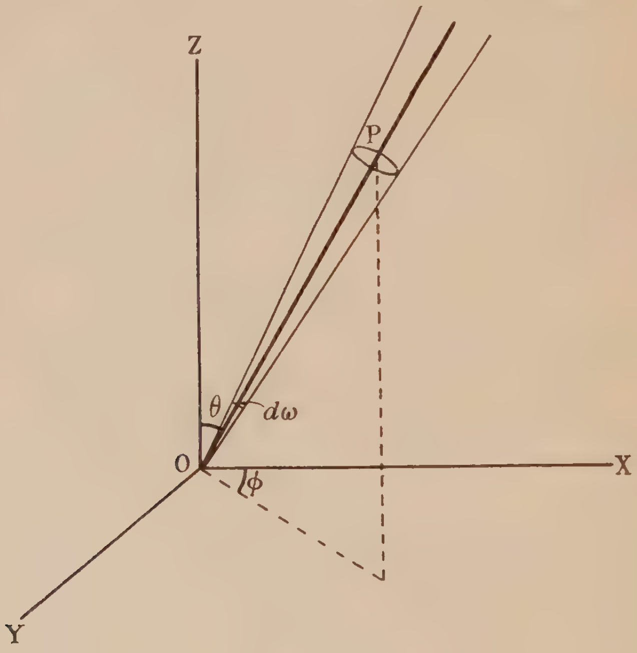

FIG. 2.

$$\frac{i \,.\, d\omega}{r^2 \,.\, d\omega} = \frac{i}{r^2} \quad . \quad . \quad . \quad . \quad (2)$$

On the other hand, the intensity of illumination of $A'B'$ is only $\frac{i \cos \psi}{r^2}$ since $A'B'$ receives exactly the same amount of energy as AB but its area is equal to $\frac{AB}{\cos \psi}$, where ψ is the angle between the normal to the surface $A'B'$ and the axis OP. The expression $\frac{i \cos \psi}{r^2}$ combines the *Inverse Square Law* and the *Cosine Law* for the reception of radiant energy. The intensity of illumination of a surface by a point source is inversely proportional to the square of its distance from the source and directly proportional to the cosine of the angle of incidence of the rays. When we speak loosely of the intensity of a beam of radiation at any point, we mean the intensity of illumination for normal incidence upon the hypothetical surface at the point in question.

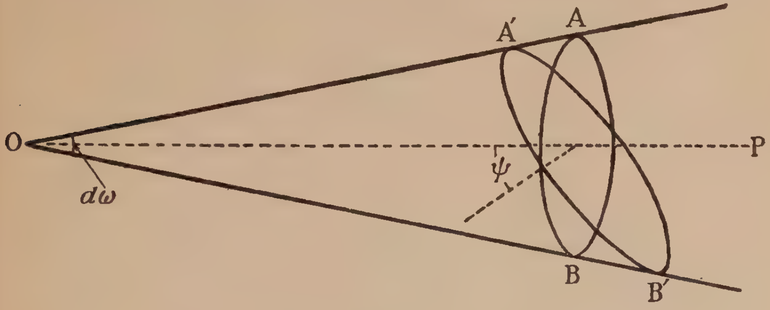

FIG. 3.

Emission from a Surface.—The emission of radiation from a surface is quantitatively expressed in terms of its *specific intensity of emission K*. This function, which is also called the *brightness* or *radiating power* of the surface, is defined by the equation

$$dE = K \,.\, ds \,.\, d\omega \quad . \quad . \quad . \quad . \quad (3)$$

wherein dE denotes the total radiant energy emitted per second by the surface element ds through the cone of solid angle $d\omega$ the axis of which is *normal* to the surface element ds. In the case of a cone of solid angle $d\omega$ drawn obliquely to ds, its direction in space is fixed by the angle θ which its axis makes with the normal to ds and by the azimuthal angle ϕ which the plane containing the axis and this normal makes with some arbitrarily fixed plane through the normal. The emission through such an oblique cone is in many cases given to a close degree of approximation by

$$dE(\theta, \phi) = K \,.\, \cos\theta \,.\, ds \,.\, d\omega \quad . \quad . \quad . \quad (4)$$

where K is independent of θ and of ϕ, and is therefore the same as for normal emission. This is the *Cosine Law of Emission* which states that the emission from a radiating surface is proportional to the cosine of the angle of observation. It is only strictly valid, however, for the radiation from a perfectly black surface. In general, the specific intensity of emission $K(\theta, \phi)$ of a radiating surface in the oblique direction (θ, ϕ) is a complex function of θ and ϕ.

If, however, we accept the Cosine Law of Emission and write

$$d\omega = \sin\theta \,.\, d\theta \,.\, d\phi$$

we obtain

$$dE(\theta, \phi) = K \,.\, \cos\theta \,.\, \sin\theta \,.\, d\theta \,.\, d\phi \,.\, ds \quad . \quad . \quad (5)$$

and by integrating this from $\theta = 0$ to $\theta = \frac{\pi}{2}$ and from $\phi = 0$ to $\phi = \pi$ we get the total emission of radiant energy per second from the surface element ds into its upper hemisphere of space. This is equal to $\pi K \, . \, ds$. The quantity $e = \pi K$, which is termed the *emissive power* of the surface, is the total energy emitted outwards in all positive directions in unit time by unit element of surface. It should be noted, however, that this simple form of expression of e in terms of K is only justified under the condition imposed, namely that the Cosine Law of Emission is valid.

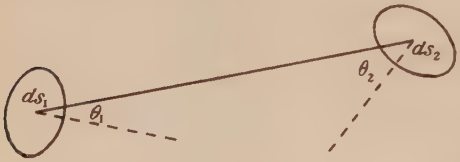

FIG. 4.

Let us now calculate the amount of radiant energy which any surface element ds_2 receives in unit time from the emitting surface element ds_1. The solid angle which ds_2 subtends at any point of ds_1 is given by

$$d\omega = \frac{\cos \theta_2 \, . \, ds_2}{r^2}.$$

The energy received per second by ds_2 is then the energy emitted per second by ds_1 within this solid angle, and, assuming the validity of the Cosine Law, this is given by

$$\begin{aligned} dE &= K \, . \cos \theta_1 \, . \, ds_1 \, . \, d\omega \\ &= \frac{K \, . \cos \theta_1 \, . \cos \theta_2}{r^2} \, . \, ds_1 \, . \, ds_2 \quad . \quad . \quad . \quad (6) \end{aligned}$$

To obtain the total radiant energy received from a radiating surface of finite dimensions by a receiving surface of finite dimensions, this expression must be integrated over both surfaces.

Hitherto we have not explicitly referred to the quality of the radiant emission. If we want to take this into account, then we must regard the specific intensity of emission K as compounded of separate contributions from all the frequencies appearing in the spectrum of the emission. Denoting that part of the total brightness K due to the infinitesimal spectral range between the frequencies ν and $\nu + d\nu$ by $K_\nu d\nu$, then

$$K = \int_0^\infty K_\nu d\nu \quad . \quad . \quad . \quad . \quad (7)$$

The quantity K_ν is termed the specific intensity of the emission for the frequency ν. It depends in general upon all the variables which determine K and also upon ν itself. Note that $K_\nu d\nu$ and not K_ν itself is of the same physical dimensions as K. If we choose to refer to the quality of the radiation in terms of wave-lengths instead of frequencies, we use the alternative expression $E_\lambda d\lambda$ as the contribution given by the wave-lengths between λ and $\lambda + d\lambda$. If the limits of the wave-length interval $d\lambda$ correspond to those of the frequency interval $d\nu$, then

$$E_\lambda d\lambda = K_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad (8)$$

However E_λ is not equal to K_ν. Instead, since $\lambda\nu = c$, we have

$$\lambda d\lambda + \nu d\nu = 0$$

or

$$|d\nu| = \left|\frac{\lambda^2 d\lambda}{c}\right|$$

and therefore

$$E_\lambda = \frac{c}{\lambda^2} . K_\nu = \frac{\nu^2}{c} . K_\nu \quad . \quad . \quad . \quad (9)$$

The plot of K_ν against ν is the quantitative mode of representation of the emission spectrum of the source.

Field Intensity.—The intensity of a field of radiant energy is defined in an analogous way to the intensity of emission from a material surface. Consider an imaginary element of surface ds within the field; in general this is traversed by radiation coming from all directions in space. The surface element can be imagined as emitting all the radiation which traverses it. Specifying a given direction as before by the angles (θ, ϕ), the radiant energy passing in unit time through the surface element in the direction (θ, ϕ) and within a cone of angle $d\omega$ is then

$$K . \cos\theta . ds . d\omega = K . \sin\theta . \cos\theta . d\theta . d\phi . ds,$$

where K is the specific intensity or brightness of the field at the point of situation of ds and in the direction (θ, ϕ). In general, K is a function of θ and ϕ, that is, the Cosine Law is not necessarily valid here either. Definitions of K_ν and E_λ for the field at any point are obtained in the same way.

In practice we aim as far as possible to use a uniform parallel directed beam of radiation, realised from a divergent or convergent beam by lens systems, collimators, and diaphragms. The intensity of such a beam of radiation is simply defined as the amount of radiant energy flowing per second through unit area of its cross-section. This is usually represented by the symbol I.

The opposite extreme to the parallel directed beam is the field of radiation which is uniformly distributed in all directions, and for which K is by definition a constant independent of θ and ϕ. In this case we can legitimately speak of the *volume density* of the radiation, meaning thereby the total amount of radiant energy which is contained in any unit volume of the field. The volume density of the radiation can easily be computed by summing the energy flux through any element of volume over all possible directions of inflow. Without detailing the mathematical steps, it results that

$$u = \frac{4\pi K}{q} \quad . \quad . \quad . \quad . \quad (10)$$

where u is the volume density of the radiation and q is the velocity of propagation of the radiation in the medium under consideration. If we wish to speak of the volume density of the radiation within a parallel directed beam of radiation of intensity I, this volume density is equal to I/q, since the amount of energy I which passes per second through unit cross-section of the beam is the total amount of radiant energy contained in a tube of this cross-section and length q cm.

ABSORPTION OF RADIATION.

Fresnel's Law.—When a surface of optical discontinuity is interposed in the path of a beam of radiation, a portion of the radiation may penetrate this surface, but there is always some part of the radiation reflected back. For a parallel beam of monochromatic light incident at right angles to the plane surface separating two material media, the fraction R of the radiation which is thus reflected is given by *Fresnel's Law*, viz.

$$R = \left(\frac{n - 1}{n + 2}\right)^2 \quad . \quad . \quad . \quad . \quad (11)$$

where n is the ratio of the refractive indices of the two media for light of the given wave-length. The fraction $(1 - R)$ which penetrates the surface may be transmitted without further loss of intensity as it passes through the second medium or it may suffer absorption or scattering. In general, however, the amount of radiation of the optical range of frequencies which is scattered by homogeneous systems may be neglected.* The radiant energy absorbed may be used to effect a variety of processes such as photo-ionisation, photochemical action, or photoluminescence in the system, or it may simply be degraded into heat energy. For the moment, however, we are not concerned with the fate of the radiant energy after it is absorbed from the directed beam but only with the possibility of expressing the absorption capacity of the medium quantitatively.

Lambert's Law.—Keeping to the case in which a parallel beam of monochromatic light is used, and denoting by I_0 the intensity of the beam just inside the surface of the absorbing system (so that the partial reflection occurring at the surface is already allowed for), *Lambert's Law* states that the fractional diminution in the intensity of the beam after traversing a given distance in the material medium is independent of I_0 and that the fractional rate of diminution in intensity with increasing penetration is constant. We have then

$$-\frac{1}{I} \cdot \frac{dI}{dx} = k \quad . \quad . \quad . \quad . \quad (12)$$

where $-dI$ is the decrease in intensity caused by the passage through a layer dx, and k is a constant called the *coefficient of absorption*

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* When colloidal matter or a fine precipitate is present, the light which is dissipated by scattering may be of significance in photochemical reactions.

(absorption coefficient). Integration between the limits $x = 0$ and $x = d$ yields

$$I_d = I_0 e^{-kd} \quad \text{or} \quad \log_e \frac{I_0}{I_d} = kd \qquad . \quad . \quad . \quad (13)$$

in which I_d = intensity at a distance d from the place of entry of the light. [In the electromagnetic theory of light, use is made of a different constant, the *index of absorption* (k'), which is related to the k above defined by the equation

$$k = \frac{4\pi k' n}{\lambda},$$

where n = refractive index of medium, and λ = wave-length of the light (*in vacuo*).] The above formula is very frequently employed in a different form by substituting decadic in place of natural logarithms. Then

$$I_d = I_0 10^{-\epsilon d} \quad \text{or} \quad \log_{10} \frac{I_0}{I_d} = \epsilon d \qquad . \quad . \quad . \quad (14)$$

the constant ϵ being termed the *extinction coefficient*. Finally, certain authors have preferred to use the *transmission coefficient* (β) as given by

$$\frac{I_d}{I_0} = \beta^d \qquad . \quad . \quad . \quad . \quad . \quad (15)$$

in which therefore

$$\beta = e^{-k} = 10^{-\epsilon} \qquad . \quad . \quad . \quad . \quad (16)$$

Lambert's Law and its corollaries are strictly valid only for monochromatic light, but they will be approximately true also for the variation of the total intensity of a beam of mixed light with depth of penetration, provided the absorption coefficient of the substance under examination changes only slightly with λ over the wave-length range involved. In general, however, k (and therefore also the related coefficients k', ϵ, and β) may vary very greatly with wave-length. The plot of k_λ or ϵ_λ against λ is the *absorption spectrum* of the substance, and this gives a true picture of the dependence of the absorption capacity of the substance upon the wave-length of the light employed. Using a continuous source of illumination, a rough idea of the positions of the regions of selective absorption can, of course, be obtained from a cursory examination of the spectrum of the emergent beam, but it is necessary to make a detailed comparison of the distribution of intensity with wave-length in this spectrum with that in the spectrum of the incident beam, and also to take into account the depth of the absorbing layer, before the true absorption spectrum can be mapped. There are various spectrophotometric devices which facilitate this procedure in practice.

Beer's Law.—For absorbing substances dissolved in transparent solvents or for absorbing gases, *Beer's Law* may be valid. This states that the value of the absorption (or extinction) coefficient is proportional to the concentration (c) of the absorbing material. We then obtain

$$k = \alpha c \quad \text{or} \quad I_d = I_0 \, . \, e^{-\alpha c d} \qquad . \quad . \quad . \quad (17)$$

and

$$\epsilon = \epsilon_m c \quad \text{or} \quad I_d = I_0 \, . \, 10^{-\epsilon_m c d} \qquad . \quad . \quad (18)$$

in which α and ϵ_m are respectively the *molecular absorption coefficient* and *molecular extinction coefficient.* The units employed are usually d in cm. and c in moles/litre.

There appear to be no standard designations for these constants, neither is there a universally recognised set of symbols, and doubt occasionally arises in reading the literature as to whether decadic or natural logarithms have been employed and as to whether or not the molecular absorption coefficient has been abbreviated to absorption coefficient. While for solutions the values given in the literature are most often molecular absorption (or extinction) coefficients, for gases it is customary to use the extinction coefficient $\left(\epsilon = \frac{1}{d} \log_{10} \frac{I_0}{I_d}\right)$ for the gas under standard conditions of temperature and pressure.

Lambert's Law must be regarded as generally true when the absorbing substance is homogeneous and suffers no chemical change on illumination. On the other hand many exceptions to Beer's Law are found in practice, especially for absorption in liquid solution. Deviations from Beer's Law are important from a photochemical standpoint, though the number of systems which have been critically studied in this connexion is not large. Variations in the molecular absorption coefficient with increasing concentration or on addition of non-absorbing substances are in general to be attributed to changes in the molecular state of the absorbing substance. These may either be definitely "chemical" changes such as polymerisation, dissociation, and complex ion formation, or "physical" changes such as solvation and interionic effects in the case of strong electrolytes. It is clear that for any substance Beer's Law can be applicable only over a limited range in much the same way as Boyle's Law and Henry's Law for gases. For example, for aqueous solutions of sodium nitrate, Beer's Law holds (for light of wave-length 303 $\mu\mu$) within 0·4 per cent. for concentrations between 0·002 N and 0·5 N; at higher concentrations, the molecular extinction coefficient falls, and a similar effect is noted when to weak solutions of $NaNO_3$ strong electrolytes such as KCl, NaCl, and $CaCl_2$ are added.

TYPES OF SPECTRA.

Emission spectra always depend to some extent upon their mode of excitation, and both emission and absorption spectra depend markedly upon the chemical nature and the physical condition of the substance concerned. A certain reciprocity always obtains between the emission and the absorption of radiation by a substance in the sense that a substance can only absorb the radiation which under favourable conditions it is also capable of emitting. This reciprocity, which is of course very important in relation to the ultimate mechanisms of the sub-atomic processes concerned, need not, however, be stressed at the moment, especially as the emission spectrum of a substance always depends upon its mode of excitation. Apart from other characteristics, spectra, whether in emission or in absorption, divide themselves into three classes—*continuous*, *series*, and *band* spectra. We shall discuss the nature of these types of spectra chiefly in relation to emission.

A continuous spectrum may represent general emission over the complete range of spectral frequencies, or the region of continuous emission may be restricted within a more or less broad spectral interval. Within the continuous region, however, no amount of dispersion available in practice suffices to resolve the emission into bright lines separated by dark spaces. Continuous emission over the whole spectrum is confined practically to the temperature radiation of matter in the solid and liquid states of aggregation. Theory relates this continuity to the interaction of the atoms or molecules upon one another in the condensed state, which results in an almost continuous variability in the condition of the very large number of atomic or molecular units which are emitting radiation at any instant, and a similar continuous variability with time in the condition of each individual unit in the system. With other modes of excitation of the solid or liquid, the emission spectrum usually consists of several regions of selective continuous emission, the positions and spectral limits of which regions depend to a large extent upon the chemical nature of the emitting substance.

The *absorption* spectra of solids and liquids consist of broad continuous selective regions of a similar nature. For most gases and vapours at high pressures, the emission and absorption spectra are also continuous, but usually there are definite signs of a more detailed structure emerging. At low pressures the emission or absorption of a gas or vapour becomes refined into a line series or a band spectrum, the detailed structure of which is specially characteristic of the chemical nature of the emitting and absorbing units which are involved.* We proceed to discuss the mathematical laws to which the detailed structures of series spectra and band spectra conform.

SERIES SPECTRA.

The Series Law.—Series emission spectra consist, with moderate dispersion, of a number of bright lines each of narrow spectral width, the wave-lengths or frequencies of which obey certain well-defined series laws. In one of the simplest cases of a spectral series, the

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* Regions of true continuous emission and absorption are also encountered in the spectra of gases and vapours at low pressures. The significance of these is discussed later.

Balmer series of hydrogen as given by the visible discharge from a Geissler tube containing hydrogen, the emission consists of a small number of sharp bright lines stretching from the red into the near ultra-violet with rapidly diminishing spacing between the consecutive lines. The frequencies of these lines conform very accurately to a mathematical relation the nature of which was first perceived by Balmer. They form the series

$$\nu = R\left\{\frac{1}{n'^2} - \frac{1}{n''^2}\right\} \quad . \quad . \quad . \quad . \quad (19)$$

where R is a constant called the Rydberg constant, $n' = 2$, and $n'' = 3, 4, 5$, etc. for successive lines of the progression. Similarly, the Lyman and Paschen series of hydrogen emission lines, also observable in the Geissler tube discharge and lying exclusively in the ultra-violet and infra-red parts of the spectrum respectively, conform to the equally simple series laws

$$\nu = R\left\{\frac{1}{1^2} - \frac{1}{n''^2}\right\}; \; n'' = 2, 3, 4 \ldots$$

and

$$\nu = R\left\{\frac{1}{3^2} - \frac{1}{n''^2}\right\}; \; n'' = 4, 5, 6 \ldots$$

These series of lines in the hydrogen spectrum are peculiarly simple numerically, and further the different series of lines lie in distinctly different regions of the spectrum so that there is no difficulty in deciding to what particular series any selected line belongs. In general, however, series spectra obtained by the usual modes of excitation consist of a very large number of lines which to the superficial view exhibit no apparent order in their spectral distribution. Detailed examination according to well-developed rules has made it possible in very many cases to resolve the complexity of lines into a number of series. The complete spectrum owes its complex appearance to the intermingling of the various series of lines. In each resolved series, the constituent lines always accumulate towards the short wave-length end, as in the various hydrogen series above. Further, although the series law is scarcely ever as simple numerically as in the case of hydrogen, the general series law possesses certain very significant characteristics. In every line spectrum which has been resolved into series, it is found that the frequency of every line of the spectrum can be expressed as the difference between two terms, and with certain exceptions each difference between *any* pair of such terms is the frequency of an observed line. This is the Ritz Principle of Combination which is of immense practical utility in the analysis of series spectra—the sorting out of the medley of lines usually observed in any spectrum into series. That the Principle possesses something more than mere arithmetical significance is proved by the fact that the number of spectral terms into which the totality of lines in any given series spectrum may be resolved is usually appreciably less than the number of lines themselves. This may readily be appreciated by reference to the case of hydrogen, for which all the lines of the Lyman, Balmer, and Paschen series are expressed as differences of the spectral terms :—

$$\frac{R}{1^2}, \frac{R}{2^2}, \frac{R}{3^2}, \frac{R}{4^2} \ldots$$

As in the case of hydrogen, each series of lines in the complete series spectrum of an element is expressed as the difference between a *constant* and a *variable* spectral term. Of the various algebraic forms of series law which have been proposed, we need only consider that of Rydberg, which states that the frequencies of successive lines in any particular series are given to a close approximation by

$$\nu = A - \frac{B}{(\mathrm{n} + \mu)^2} \quad . \quad . \quad . \quad . \quad (20)$$

Here A is the constant term of the series—it is actually the frequency of the series convergence limit. B and μ are also constants for the series, and n is a variable whole number—the *serial number*—which increases successively by one unit as we go up the series (increasing ν). The constant B is either equal to the Rydberg constant R in the series spectrum of hydrogen, or it is four, nine, or in a few cases sixteen times this quantity. The particular value of B determines the *order* of spectrum to which the series belongs.

Arc and Spark Spectra.—Modern theory identifies the atom, whether neutral or ionised, as the seat of the emission of series spectra. The usual modes of excitation are electrical, but the flame and furnace spectra of most of the elements which are monatomic under the conditions of excitation, in especial of the metals, are series spectra, although only one or two series lines are obtained unless the temperature of the flame or furnace is very high. In general, however, for electrical excitation of the spectrum, if any line of a particular series is emitted, most or all of the lines of that series simultaneously appear, the intensity of the lines diminishing as we pass towards the convergence limit. Excitation of an element by the flame, the furnace, or the electric arc gives rise principally to what we call the *arc spectrum* of the element. The much more violent disturbances in the atom occasioned by the condensed spark discharge produces the *spark spectrum* of the element. In this, certain lines which may also be present with feeble intensity in the arc spectrum, but which are not embraced by the various series of the main arc lines, are greatly enhanced in intensity, and fresh lines, not present in the arc spectrum, also appear. For all the lines of the arc spectrum which are not enhanced by passing from the conditions of the arc to those of the spark, the factor B has the same value as the Rydberg constant R. On the other hand, the majority of the lines in the spark spectrum are expressed by series formulæ in which the value of B is four times the Rydberg constant; the spectrum made up of these lines is alternatively called the enhanced spectrum of the first order. Under certain extreme conditions, lines are obtained by the spark discharge which belong to enhanced spectra of the second and third orders, and for which the values of B are numerically nine and sixteen times the Rydberg constant respectively.

The seat of emission of the lines of the arc spectrum is now known to be the neutral atom; that of the spark spectrum, or rather of those series in the spark spectrum which constitute the enhanced spectrum of the first order, is the singly ionised atom; and correspondingly, the emitter of any line of the enhanced spectrum of the xth order is the ionised atom which has been stripped of x of its outer electrons. The physical evidence for these conclusions is dealt with in Chapter II.

The Spectral Terms.—The various series in the complete series spectrum of any given order of an element are classified according to the values of the constant term A and of the constant μ in the variable term of equation (20). Confining ourselves to the arc spectrum—the same general rules apply, however, to any series spectrum of higher order—it is found that the majority of the lines arrange themselves into four distinct series which are called the Principal, the First Subsidiary or Diffuse, the Second Subsidiary or Sharp, and the Bergmann or Fundamental Series. These series are primarily characterised by four distinct and different values of the series constant μ in the variable terms. These different values of μ are, in general, represented by the symbols P, D, S, and F and the variable terms in the above series by $\mathrm{n}P$, $\mathrm{n}D$, $\mathrm{n}S$, and $\mathrm{n}F$ respectively. Thus the term $\mathrm{n}P$ is numerically equal to $\frac{R}{(\mathrm{n}+P)^2}$, the term $\mathrm{n}D$ to $\frac{R}{(\mathrm{n}+D)^2}$, etc. The frequencies of the various lines of the four series, when resolved into differences of terms, are then given by :—

Principal $\nu = P_\infty - \mathrm{n}P$; $\mathrm{n} = 2, 3, 4, 5 \ldots$
1st Subsidiary $\nu = D_\infty - \mathrm{n}D$; $\mathrm{n} = 3, 4, 5, 6 \ldots$
2nd Subsidiary $\nu = S_\infty - \mathrm{n}S$; $\mathrm{n} = 2, 3, 4, 5 \ldots$
Fundamental $\nu = F_\infty - \mathrm{n}F$; $\mathrm{n} = 4, 5, 6, 7 \ldots$

Here the constant terms P_∞, D_∞, S_∞, and F_∞ are obviously the frequencies corresponding to the series convergence limits. In conformity with the Ritz Principle of Combination these constant terms now fall into the general scheme of spectral terms in the following manner. It is found that the convergence limit of the Principal Series is numerically identical with the first term ($\mathrm{n} = 1$) in the *sequence of terms* * represented by $\mathrm{n}S$; the first and second Subsidiary Series have a common convergence limit which is numerically equal to the term $2P$; and the convergence limit of the Bergmann Series is the term $\mathrm{n}D$ for which $\mathrm{n} = 3$. The four main series of lines can therefore be rewritten in the following way :—

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* In general we will speak of a *series* of lines and a *sequence* of terms. S, P, D, F may be referred to either as series constants or sequence constants, and n as the sequence variable or the serial number.

Principal $\nu = 1S - nP$; $n = 2, 3, 4, 5, 6 \ldots$
1st Subsidiary $\nu = 2P - nD$; $n = 3, 4, 5, 6, 7 \ldots$
2nd Subsidiary $\nu = 2P - nS$; $n = 2, 3, 4, 5, 6 \ldots$
Fundamental $\nu = 3D - nF$; $n = 4, 5, 6, 7, 8 \ldots$

These are the series of most frequent occurrence in line spectra. Other series which are, however, occasionally met with are given by the combinations :—

$\nu = 2S - nP$; $n = 3, 4, 5, 6 \ldots\ldots$
$\nu = 3P - nD$; $n = 4, 5, 6, 7 \ldots\ldots$
$\nu = 3D - nP$; $n = 4, 5, 6, 7 \ldots\ldots$
and $\nu = 4F - nD$; $n = 5, 6, 7, 8 \ldots\ldots$

If the spectral terms, instead of the spectral lines, be arranged in order of descending magnitude, we obtain the *S*, *P*, *D*, and *F* sequences of terms and the *term system* :—*

1*S*	2*S*	3*S*	4*S*	5*S*	6*S*	...	...
	2*P*	3*P*	4*P*	5*P*	6*P*	...	...
		3*D*	4*D*	5*D*	6*D*	...	...
			4*F*	5*F*	6*F*	...	...
				...	...	...	...
					...	...	...

The term sequences have here been arranged in the order *S*, *P*, *D*, *F* to illustrate an important restriction to the Ritz Principle of Combination which is found to obtain in practice. According to this Principle we should expect to find spectral lines represented by the term combinations $(S - D)$ and $(S - F)$. The normally observed possibilities of term combination are, however, limited by the rules :—

(*a*) Two terms of the same sequence, e.g. two *S* terms, do not combine with one another.

(*b*) The *S* terms only combine with *P* terms, the *P* terms only with *S* and with *D* terms, the *D* terms only with *P* and with *F* terms.

It will be seen from this that a term belonging to any sequence combines only with terms in the sequence immediately above or immediately below it. Whilst spectral lines which afford exceptions to these rules are occasionally met with, it is found that such lines are only produced under abnormal conditions of excitation of the atom. The rules possess an important theoretical significance which will be dealt with later.

We must refer briefly here to the above system of enumeration of the series of lines or sequences of terms with respect to the serial number n. Since the absolute value of the constant *S*, *P*, *D*, or *F* in any sequence of terms is undetermined until the value of n for one term is fixed, it might seem equally justifiable, for example, to write the largest (first) of the *P* sequence of terms as 1*P* instead of 2*P* and the complete sequence as $1P$, $2P$, $3P$. . . . This would merely require the empirical constant P to be increased throughout by one unit. Actually, this and other methods of notation have been suggested and employed in spectroscopic usage; for example, the sequence of S terms has alternatively been designated by $1{\cdot}5S$, $2{\cdot}5S$, $3{\cdot}5S$. . . . The notation which we use above has the virtue of simplicity but has little theoretical basis. Its only real justification lies in the fact that the thereby fixed values of the series constants S, P, D, F decrease in this order (which is the order of their combination) in the case of many of the simpler elements, and that the resulting values of D and F are in few cases different from zero by more than a few per cent. Actually, in terms of the modern interpretation of the spectral terms, the values 3 and 4, ascribed to the serial number n of the largest D and F terms respectively, usually have a real physical significance. The same does not in general apply, however, to the serial numbers which we have ascribed to the S and P terms.

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* In addition to the *S*, *P*, *D*, and *F* terms, lines are occasionally observed in series spectra which involve *G* and *H* terms.

Multiplet Structure of Spectral Lines.—So far, it has been assumed that the constituent lines of any of the above spectral series are single emission lines. More often than not, however, in line series spectra the individual numbers of the various series each possess a multiplet structure—the " lines " may be doublets, triplets, quartets, etc. Individual " lines " which are composite of as many as eighteen components have been observed. The sodium D line, which with moderately good dispersion is seen to consist of the two separate lines of wave-lengths 5890 and 5896 Å, is the familiar example of doublet structure. In this case, the doublet separation is comparatively small, but this is not a general characteristic of multiplet structure; in many instances the components of the complex line are widely separated spectrally, so that other lines belonging to entirely different series of the spectrum may lie between the associated components.

The first fact to be noted about multiplet systems of lines is that, if one member of a spectral series is a doublet, all the other lines of the same series are likewise doublets; similarly for triplets and multiplicities of higher order. Again, for the various series of multiplet lines in the spectrum of an element certain simple rules are found to apply. Suppose we are dealing with the doublet series which occur in the *arc spectrum of any of the alkali metals*. Then for the First and Second Subsidiary Series of " lines," the separation of the components of each doublet, when expressed as a frequency or wave-number, is a constant, independent of the serial number n of the line. This constant separation is the same in both the sharp and the diffuse series, and further it is equal to the separation of the two components of the first doublet in the Principal Series of lines. On the other hand, the doublet separation in the Principal Series decreases progressively to zero as the serial number n increases; in other words, the two partial series of lines formed from homologous components of the doublets of the Principal Series converge to the same series limit in the ultra-violet. These rules apply equally to series of lines of higher multiplicity.

Such experimental observations as these are easily understood when the multiplet structure of each spectral line is referred to a multiplicity of the spectral terms which combine to give the line. Corresponding to the multiplet structure of the arc spectrum of any alkali metal, the S, P, D, F system of terms into which the frequencies of the lines are resolved form a *doublet system of terms.*

In such a doublet system of terms all the S terms are singlets (this is a general rule for the S terms of all series spectra), but all the P, D, and F terms are doublets. For each serial number n there are thus two partial P terms, which differ numerically only in the value of the constant P in the Rydberg expression for the term $\frac{R}{(\mathrm{n}+P)^2}$; similarly for the two partial D terms and the two partial F terms corresponding to each value of n. We represent the complete doublet system of terms by the notation :—

$$\mathrm{n}^2S_1;\ \mathrm{n}^2P_1,\ \mathrm{n}^2P_2;\ \mathrm{n}^2D_2,\ \mathrm{n}^2D_3;\ \mathrm{n}^2F_3,\ \mathrm{n}^2F_4.$$

By this method of notation,* the central symbol in the representation of the term is the letter S, P, D, or F which characterises the sequence to which it belongs. The multiplicity of the system is indicated by the upper index to the left of the sequence letter (note that the S terms, though themselves singlets, belong to a doublet *system* of terms). The component of the multiple term is indicated by the suffix † to the right. Finally, the serial number is denoted as heretofore by an integer n prefixed to the main symbol. In the case of singlet terms, and also for multiple terms where the components of the term are too close to resolve, the lower index may be dropped, e.g. the S sequence of terms above may be written as n^2S. Whether or not the suffix be dropped, however, it is usually politic to retain the upper index which identifies the system to which the term belongs.

Returning to the arc spectra of the alkali metals, we now see that the Principal Series of lines is represented as the difference of a constant singlet term 1^2S_1 and a variable doublet term $\mathrm{n}^2P_{1,2}$, giving the two partial series of lines $\nu = 1^2S_1 - \mathrm{n}^2P_1$ and $\nu = 1^2S_1 - \mathrm{n}^2P_2$.

---

* Until recently there has been no general agreement among spectroscopists regarding a common system of notation of spectral terms and especially of multiple terms, and considerable confusion arises out of the different methods of momenclature of Paschen, Fowler, Sommerfeld, etc. The notation we have adopted here is that due to Russell and Saunders (*Astrophys. J.*, **61**, 38, 1925). On account of its simplicity and comprehensiveness, it has already attracted a large following among spectroscopic workers, and there is every indication that it will assume general use in the near future.

† It would be out of place here to attempt to explain why these suffices are enumerated in the manner just given. We need only remark at the moment that the enumeration is not arbitrary, the values of the subscripts given being determined by the inner quantum numbers of the atomic states to which the spectral terms correspond (cf. Chapter II., pp. 97-106). It should be noted that the numerically smaller component of each doublet term is represented by the larger value of the suffix, so that $\mathrm{n}^2P_1 > \mathrm{n}^2P_2$, $\mathrm{n}^2D_2 > \mathrm{n}^2D_3$, and $\mathrm{n}^2F_3 > \mathrm{n}^2F_4$.

From this it is immediately clear why the doublet separation, which is given by

$$n^2P_1 - n^2P_2 = R\left\{\frac{1}{(n+P_1)^2} - \frac{1}{(n+P_2)^2}\right\},$$

should progressively decrease in value to zero as the variable serial number n of the doublet line increases. On the other hand, the Second Subsidiary Series, viz. $\nu = 2^2P_{1,2} - n^2S_1$, represents the difference between a constant doublet term and a varying singlet term, hence the series is a series of doublets with the constant separation $(2^2P_1 - 2^2P_2)$, which is also the separation of the two components in the first $(n = 2)$ doublet of the Principal Series. The First Subsidiary Series of lines in the arc spectrum of lithium and of sodium also appears as a series of doublets of constant separation, equal in magnitude to that in the Second Subsidiary Series. This doublet structure owes its origin also to the multiple nature of the first term in the expression $\nu = 2^2P_{1,2} - n^2D_{2,3}$ which should represent the First Subsidiary Series. The higher multiplicity of the lines comprising this series which we should expect as a result of the complexity of the D term is masked, for the lighter alkali metals, by the very small differences in the values of the partial D terms. In the First Subsidiary Series of the heavier alkali metals, however, the differences of the partial D terms are larger, and we obtain a series of "composite doublets," where the lower frequency member of each doublet carries a third line, or satellite as it is called, separated from it by a frequency difference which is equal to the difference in the two partial D terms. The first member $\nu = 2^2P_{1,2} - 3^2D_{2,3}$ of this series of composite doublets appears as the full lines in Fig. 5.

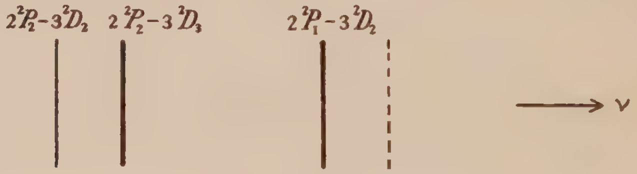
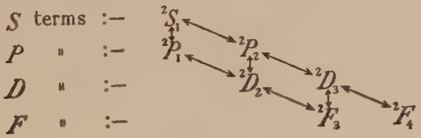


FIG. 5.

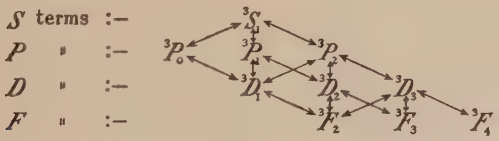
There should, however, be another spectral line of frequency $\nu = 2^2P_1 - 3^2D_3$, at the position marked by the dotted line in the figure, in order to complete the four lines which all the possible algebraic combinations of two doublet terms would give, but this fourth line is not observed in practice. Its absence provides an instance of a further restriction which is found to govern the possibilities of combination of terms to give emission lines. It has already been stated that an S term combines normally only with a P term, a P term only with an S or with a D term, and a D term only with a P or with an F term. When the terms are multiplets the possibilities of combination of the components or partial terms with one another are governed by this same rule, but in addition *the suffix numerals of the two combining terms can only differ by* 0 *or* ± 1. Writing the terms as in the scheme below, all the possibilities of combination of the partial terms with one another to give spectral lines are indicated by the arrows.



Turning now to the *arc spectrum of any of the elements of Group II.* of the Periodic Classification, we find here a much greater complexity of spectral terms. The various sequences of terms now divide themselves into *two distinct systems*, the one a singlet system, which we designate by the symbols $^1S_0, ^1P_1, ^1D_2$, and $^1F_3$, the other a triplet system of terms represented by the scheme:—

$$^3S_1\,;\;\; ^3P_0, ^3P_1, ^3P_2\,;\;\; ^3D_1, ^3D_2, ^3D_3\,;\;\; ^3F_2, ^3F_3, ^3F_4.$$

In the triplet system of terms, the S terms are singlets (but very different in value from the S terms of the singlet system), while the P, D, and F terms are all triplets. The terms of the singlet system combine with one another to give spectral lines in accordance with the restriction already stated, viz. the combinations permitted are $^1S_0$ with $^1P_1$ terms, $^1P_1$ with $^1D_2$ terms, and $^1D_2$ with $^1F_3$ terms. The terms of the triplet system also combine with one another according to a restriction principle identical with that already stated in connection with the doublet system of the alkali metals. The various possible combinations are indicated by the arrows in the scheme:—



We can have two entirely different Principal Series of lines in the arc spectrum of any element of Group II. The one Principal Series is a series of single lines represented by the formula $\nu = 1^1S_0 - n^1P_1$ or more concisely by $\nu = 1^1S - n^1P$. The other Principal Series of spectral lines is a series of triplets given by the formula

$$\nu = 1^3S_1 - n^3P_{0,1,2}.$$

Similarly we can have two 1st Subsidiary Series of lines, the one a series of single lines with frequencies given by $\nu = 2^1P - n^1D$, the other a series of sextets whose frequencies are those of the combinations $\nu = 2^3P_{0,1,2} - n^3D_{1,2,3}$ which are permitted by the scheme given above.

Besides these types of combination within each system of terms, there are also various possibilities of *inter-combination of the two systems*. Thus the ^1S terms may combine with the ^3P terms, the ^3S terms with the ^1P terms, and so on. Such inter-combinations are limited by the same restrictions as apply to the combinations within one system, with the additional reservation, however, that terms of suffix zero do not combine with one another. Lines of frequent occurrence in the arc spectra of the elements of Group II. are those given by the combination $(1^1S - n^3P)$. In spite of the triplet nature of the ^3P terms, however, the observed lines are only singlets, being the components represented by $(1^1S_0 - n^3P_1)$. The combinations of the 1^1S_0 term with n^3P_0 and n^3P_2 are both forbidden.

We have seen that the maximum term multiplicity in the arc spectrum of the alkali metals is two, and that it rises to three in the case of metals of Group II. As we pass from left to right of the periodic table of elements, even higher multiplicities appear. For example, the element scandium has not only a doublet system of terms, but also a quartet system; while titanium has a system of triplet terms and a system of quintet terms. The element manganese has three term systems, of quartets, sextets, and octets respectively; iron has also three term systems—triplets, quintets, and septets. The extremely complex line spectra given by the metals of Groups VII and VIII of the Periodic classification are due in part at least to these high multiplicities within each system of terms and to the occurrence of the three separate systems of terms with the resulting manifold possibilities of inter-combination.

Analysis of Line-Spectra.—By temperature excitation of an element in the flame or furnace, it is possible to produce an emission which consists of one or at most only a few lines of one series in the arc spectrum of the element. By electrical excitation, however, it is not generally possible to excite lines which belong to only one series or indeed to excite only those lines which belong to a spectrum of definite order. In such circumstances, it is obvious that the analysis into their proper series of the totality of lines which is obtained on a spectrogram must demand a large measure of skill and practice. The operation is facilitated by the use of various rules which have gradually evolved from spectroscopic practice and certain of which have already been stated in the text. In the first place, the lines of the arc and spark spectra of the same element are distinguished from one another by the relative ease with which they may be produced and enhanced. Lines belonging to spectra of still higher order are of rare occurrence and always lie well into the ultra-violet. Use may also be made of the *Law of Spectroscopic Displacement* which states that the xth order spectrum of any element bears a very close structural resemblance to the $(x - 1)$th order spectrum of the element which immediately precedes it in the atomic number sequence. Thus, when allowance is made for the fact that the "Rydberg constant" in the one case is four times as great as in the other, the spark spectrum of an element is very similar to the arc spectrum of the preceding element; if, for example, the terms of the latter spectrum constitute a doublet system, so also will the terms of the related spark spectrum. The series spectra of neutral lithium, singly ionised beryllium, doubly ionised boron, and trebly ionised carbon form an associated group of this character. The same is true of the corresponding spectra of the homologous series Na, Mg^+, Al^{++}, and Si^{+++}.

Having decided the order of spectrum to which the various lines belong, it is next necessary to assign the lines within each order to their appropriate series. It is first to be noted that the four series already dealt with, viz. the Principal, 1st Subsidiary, 2nd Subsidiary, and the Bergmann, are the most important and their lines are of most frequent occurrence. If the series formulæ of the lines belonging to these can be found, the frequencies of most other lines occurring in the same spectrum can be deduced by the Ritz Principle of Combination and identified in the spectrogram. In many cases, lines belonging to one and the same series can be picked out by examination of their physical characteristics. If the wave-numbers of lines which are believed to form a series are plotted against a series of the natural whole numbers, the graphed points should lie on a smooth curve. Usually only the first few lines of a series are emitted with appreciable intensity, and so the very important convergence frequency of the series, which is equal to the fixed term in the series formula, can only be obtained by extrapolation—graphically or by adopting a suitable series formula for the representation of the observed members of the series. This convergence frequency can afterwards be checked when other series of the spectrum have been analysed, since it must fit naturally into the system of terms by which all the series of lines are ultimately to be represented. The physical characteristics which help to distinguish the various series may now be summarised. The lines of different series sometimes differ markedly from one another as regards the sharpness of definition of their edges. Diffuseness—a term which implies a blurred or shaded appearance of one or both edges of the line—is usually associated with the lines of the 1st Subsidiary Series. On the other hand, the lines of the 2nd Subsidiary Series are generally characterised by their sharpness of definition. Since the 1st and 2nd Subsidiary Series have the same convergence limit, so that the higher members of the two occupy the same spectral region, this criterion is useful in separating and identifying the constituent lines of these two series. However, not all 1st Subsidiary Series lines are necessarily diffuse in appearance, nor is the property confined to the lines of this series alone. Diffuseness is often exhibited by the higher members of other series and in particular by lines characterised by a current D or F term. The temperature classification of lines obtained by flame, arc, or furnace excitation provides a further aid to their identification. Lines which can be excited at relatively low temperatures are usually easily reversed, that is, the line may appear as a thin *black* line with broad luminous edges, due to reabsorption of the central portion of the emission line by cooler vapour in the outer zone of the flame or arc. The Fraunhofer lines in the spectrum of the sun are the familiar examples of this phenomenon. Strong reversal is associated with the spectral lines which originate in the lowest energy level of the atom, and in a large number of cases such lines belong to the Principal Series. Accordingly, it was at one time customary to associate strong reversal with the Principal Series, but this criterion cannot be held to be generally valid. For all the elements of Groups I. and II. of the Periodic Table, the lines of the Principal Series are strongly reversed, yet in the case of other metals, such as aluminium, it is the lines of the 1st and 2nd Subsidiary Series which are reversed in the arc. These, and not the lines of the Principal Series, originate in the lowest energy level of the aluminium atom. More properly, therefore, the ease of reversal of spectral lines should be used as a guide to the condition of the atom in its normal state.

For spectral lines belonging to multiplet series, there are several useful rules, such as the law of constant doublet or triplet separation for the components of the 1st and 2nd Subsidiary Series, which help to identify the system and the series concerned. In addition to such structural peculiarities, there are also various intensity rules referring to the relative intensities of the components of compound lines. Thus, in a Principal Series of doublets the shorter wave-length component of each line has always the greater intensity, while in the corresponding Sharp and Diffuse Series (ignoring satellites) the reverse is true. A similar regularity applies to series of triplets.

Probably the surest guide in finding the series to which a spectral line belongs as well as the multiplicity of the system or systems to which its component terms belong is afforded by the completely resolved Zeeman pattern of the line. The Zeeman effect is the name given to the splitting of a simple spectral line into several components which is brought about by subjecting the radiating atom to the influence of an external magnetic field. In the so-called normal effect, the single spectral line observed in the absence of the field appears as three separate lines (cf. Fig. 6 (*a*)) when viewed in a direction perpendicular to the magnetic lines of force. The central (π) component occupies the same position as the original line and is plane polarised with the electric vector *parallel* to the magnetic lines of force; the outer (σ) components are equidistant (in the frequency or wave-number scale) from the central component and are plane polarised with the electric vector *perpendicular* to the magnetic lines of force. When viewed longitudinally, i.e. along the magnetic lines of force, only these components are visible and they are now circularly polarised in opposite directions in the plane of observation. When we speak of a Zeeman pattern, however, we usually mean the appearance of the resolved line as viewed transversely. The normal Zeeman effect is given by the lines of the arc spectrum of hydrogen, by the lines of the spark spectrum of helium, and by all singlet lines in the series spectra of the other elements. On the other hand, lines which are built up of complex terms give the so-called anomalous Zeeman effect. Here the Zeeman pattern usually contains a larger number of components, and these although symmetrically placed relative to the unresolved line are not always equally spaced. It has, however, been found possible to correlate definite Zeeman patterns with definite types of series of lines, so that conversely the Zeeman pattern can be used to determine unequivocally the type of series to which the line belongs. Each component of a complex line has its own characteristic Zeeman pattern, and the pattern is qualitatively and quantitatively the same for all homologous components of the same series.

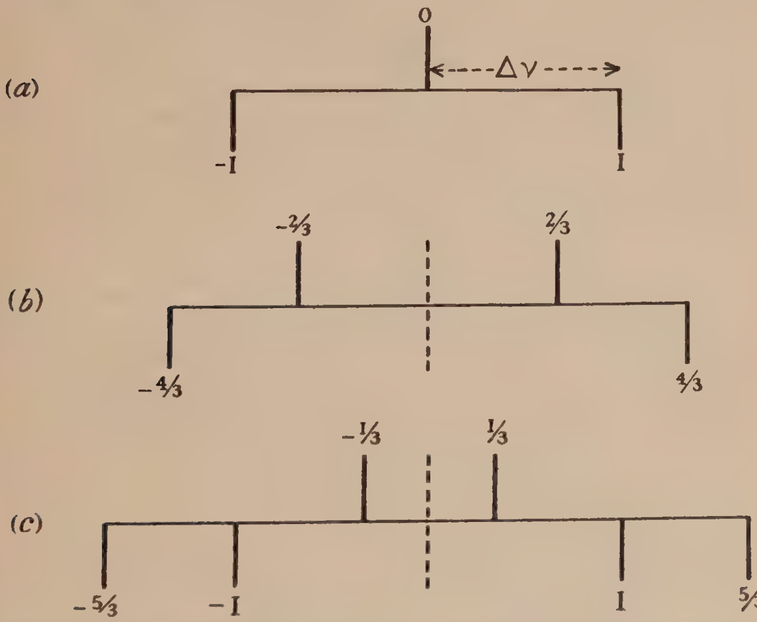


FIG. 6.—(*a*) Normal Zeeman pattern given by singlet lines; (*b*) Anomalous Zeeman pattern of $1^2S - n^2P_1$ lines; (*c*) Anomalous Zeeman pattern of $1^2S - n^2P_2$ lines.

As a simple illustration we may consider the Principal Series of doublet lines in the arc spectrum of sodium, of which the yellow $D_1 - D_2$ line is the first member. The series is represented by the formula

$$\nu = 1^2S - n^2P_{1,2}.$$

The D_1 line ($\nu = 1^2S - 2^2P_1$) is resolved under the influence of a magnetic field into four lines, two π components and two σ components, whose positions relative to the original D_1 line are as indicated in Fig. 6 (*b*).

In the figure the π components are drawn above the horizontal line, the σ components below the line. The original D_1 line is absent in the Zeemann pattern and its position is indicated by the dotted line. The pattern is drawn to scale, and the numbers attached to the various components give their displacements from the original line, the unit of displacement being taken as that of either component ($\Delta\nu$) in the normal Zeeman pattern (*a*). All the lines in the sodium spectrum represented by $\nu = 1^2S - n^2P_1$, that is the homologues of the D_1 line, have exactly the same Zeeman pattern. On the other hand, the D_2 line ($\nu = 1^2S - 2^2P_2$) and all its homologues give a Zeeman pattern consisting of two π components and four σ components, spaced as illustrated in Fig. 6 (*c*). Each of these Zeeman patterns is further characterised by definite rules which govern the relative intensities of the π and σ components. More complex Zeeman patterns are given by other series, and in general the number of Zeeman components increases with the multiplicity of the term systems which are involved in the analytical expression of the line. For further details, reference may be made to Sommerfeld, *Atomic Structure and Spectral Lines.*

BAND SPECTRA.

While series spectra are exclusively associated with the atom, whether neutral or ionised, as the emitting unit, band spectra are characteristic of molecules or of molecular ions containing more than one atom. Band spectra are conveniently divided into three classes—rotation, rotation-vibration, and electronic band spectra respectively, but it is only the last-named type which has been studied to any extent in emission. Nevertheless it will be convenient to say a few words here regarding the general features of the two simpler classes of band spectra.

Rotation Spectra.—This class of spectrum which has been studied only in absorption always lies in the extreme infra-red region, and owes its origin, as the name implies, to the conversion of the absorbed radiation into rotational energy of the absorbing unit. Since radiant energy can react only with electrically polar systems, it follows that pure rotation absorption spectra are given only by substances the molecules of which are heteropolar in nature. The homopolar molecules, such as hydrogen, oxygen, nitrogen, chlorine, etc., exhibit no absorption in the far infra-red. The absorption spectrum of hydrochloric acid in this region affords the simplest example of a pure rotation spectrum. This consists of several well-defined absorption maxima (lines) lying between 40 μ and 100 μ, the frequencies of which form an approximate arithmetic progression, with constant separation of successive maxima. This is the structural characteristic of all band spectra in the infra-red. The frequencies of the HCl absorption maxima are represented by $\nu = bm$ where b is a constant and

$$m = 5, 6, 7 \ . \ . \ . \ 11,$$

or more accurately by inclusion of a small cubic term

$$\nu = bm - dm^3 \quad . \quad . \quad . \quad . \quad (21)$$

It is to be noted that while band spectra, just as series line spectra, can be represented as functions of small whole numbers, the types of function are very different in the two cases. The only pure rotation spectrum of a polyatomic molecule which has been examined in any detail is that of water vapour. This absorption spectrum also consists (in the frequency scale) of a series of approximately equidistant maxima of absorption stretching over the region 9 μ — 180 μ.

Rotation-Vibration Spectra.—Rotation-vibration bands lie in the near infra-red region of the spectrum, and, like pure rotation bands, consist of a number of absorption maxima which to a first approximation are equally spaced in the frequency scale. Moreover, this spacing is approximately the same as that in the rotation spectrum of the same substance. The rotation-vibration spectrum, however, is not simply the continuation of the pure rotation spectrum into the near infra-red. The group of lines which form the near infra-red band possess certain features which serve to distinguish them from the pure rotation lines. Taking the near infra-red absorption spectrum of HCl as an example, this consists of a region of strong absorption stretching from 3·2 to 4·0 μ, which resolves under dispersion (cf. Fig. 7) into a large number of sub-maxima grouping themselves more or less symmetrically on either side of a central position at 3·46 μ. The frequencies of these sub-maxima form to a first approximation an arithmetic progression. More accurately, the sub-maxima to the short wave-length side of the centre of the band converge slowly, and those on the long wave-length side diverge slowly, as we pass from the centre. At the centre of the band the absorption is very slight and the spacing here is anomalous being approximately twice the spacing on either side, in other words the central line of the band is missing. The intensities of the band lines are distributed in fairly symmetrical fashion on either side of this central position. Passing from the centre towards either the far infra-red or the visible, the

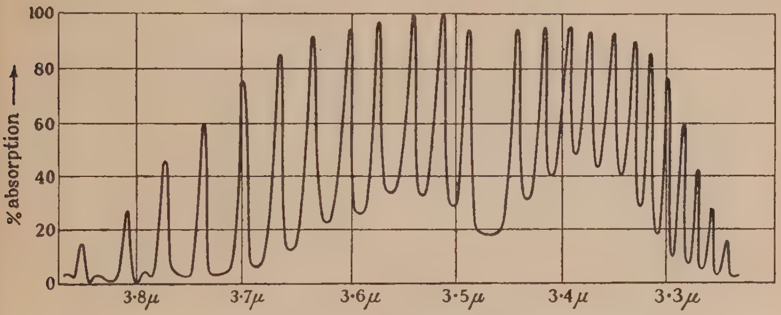


FIG. 7.—The HCl absorption band at 3·46 μ.

intensity goes through a flat maximum and then falls off to zero on either side. The frequencies of the band lines are represented approximately by

$$\nu = \nu_v \pm bm,$$

or more accurately by the inclusion of a small quadratic term

$$\nu = \nu_v \pm bm + cm^2 \quad . \quad . \quad . \quad (22)$$

Here ν_v, b, and c are constants characteristic of the band, and $m =$ 1, 2, 3, 4 . . . The positive sign gives the members lying to the right of the centre—the positive branch of the band, the $-^{ve}$ sign gives those lying to the left of the centre—the negative branch. The frequency $\nu = \nu_v$ itself gives the position of the centre of the band, at which, as already noted, a line is missing. The constant b gives the approximate spacing (in frequency units) of the first few lines in either branch. For bands, such as that of HCl, which "degrade" towards the infra-red, i.e. the lines of which diverge in this direction, the constant c in the above formula is negative in value. According to modern theory, the term ν_v which determines the spectral position of the band as a whole is a characteristic of the vibration frequency of the constituent atoms of the absorbing molecule with respect to one another. The additional terms which give to the band its fine structure result from the variable rotation of the molecule as a whole which can be superimposed upon this nuclear vibration.

Besides the absorption band of HCl at 3·46 μ there are two other absorption bands in the near infra-red at 1·76 μ and 1·19 μ. The first of these has been resolved into its constituent lines and is found to possess a fine structure essentially similar to that of the 3·46 μ band. Further, the spacing of the component lines is practically the same in the two cases. The HCl bands at 1·76 μ and 1·19 μ are to be regarded as the first and second harmonics of the fundamental band at 3·46 μ. The frequencies of their centres are approximately twice and three times that of the centre of the fundamental band. Similarly, in the near infra-red absorption spectrum of carbon monoxide, we find the three bands at 4·67 μ, 2·35 μ, and 1·57 μ, the frequencies of whose centres are also approximately in the ratio 1 : 2 : 3. Hydrobromic and hydrofluoric acids possess absorption bands in the near infra-red which are of the same simple internal structure as those of hydrochloric acid.

The absorption in the near infra-red of several polyatomic gases, notably of CO_2, H_2O vapour, NH_3, and CH_4 has been extensively investigated during the last few years. The band systems of these gases are in general of a much more complex nature than those of the heteropolar diatomic molecules, yet, for such bands as have admitted of resolution into their component lines, the arithmetic progression rule within the band has been found to be equally applicable. It should be noted here that the demonstration in practice of the fine structure of bands in the infra-red always requires a considerable degree of dispersion and appears to be feasible only when the molecule concerned contains one or more very light atoms. Thus, while the fine structure of several of the bands of the hydrogen halides, methane, water vapour, and ammonia can be obtained experimentally, the infra-red bands of carbon monoxide and of carbon dioxide are not capable of complete resolution. Carbon dioxide possesses three principal regions of absorption in the infra-red, at 2·7 μ, 4·3 μ, and 14·7 μ. The frequencies of the centres of these do not, however, appear to be connected by any simple multiple relation as are those of the band centres for carbon monoxide. The band at 4·3 μ can be partially resolved into a doublet (as would the HCl band of Fig. 7 with weak dispersion), but the best dispersion available is not sufficient to reveal the fine structure further. The absorption in the region of 2·7 μ actually consists of two bands each of which has a doublet structure under strong dispersion. Methane has several absorption bands in the near infra-red, two of which lying at 7·7 μ and 3·3 μ have been examined in detail. These reveal a striking fine structure of well-defined and almost equidistant lines. The spacing of the lines in the 3·3 μ band is almost double that of the lines in the 7·7 μ band. For water vapour, there are about a dozen absorption bands lying between 7·0 μ and 0·7 μ, the positions of which may all be represented as multiples or additive combinations of the frequencies of the two strong bands at 6·3 μ and 2·7 μ. The rotational fine structure of certain of these water vapour absorption bands has been recently investigated in detail, but, while many regularities are apparent in the spacing of the numerous lines within each band, the ultimate details have not been analysed with the same completeness as in the case of the hydrogen halides.

Electronic Band Spectra.—Molecules and molecular ions emit in the visible and in the ultra-violet a complex electronic band spectrum which under low dispersion appears as a succession of bright and fairly narrow emission bands each possessing a characteristic fluted or channelled structure. Usually each band is sharply defined on one side but diffuse on the other. The sharply defined edge of the band is called its head and this may lie either on the red or on the violet side. Correspondingly the band is said to be degraded or shaded towards the violet or towards the red. These electronic bands are really of very complicated internal structure, each resolving under high dispersion into an exceedingly large number of fine sharp lines. In the resolved band the fine lines appear to be rather irregularly placed, but the mean spacing gradually diminishes as the head is approached, and here the lines are very densely crowded together, so much so in many bands that resolution of the separate lines at the head is practically impossible. The head of a band, however, must not be regarded as the convergence of an infinity of lines, as is the convergence limit of a line series spectrum. The accumulation of the lines to form a sharp head is a characteristic physical feature of most electronic bands, but it is in a certain sense an accidental phenomenon, and that line which actually forms the head has no very special theoretical significance. The maximum of intensity within the band does not usually fall at the head itself. The emission under low dispersion appears to be brightest at the head simply because of the accumulation of lines there. In the simpler electronic bands, there may, despite the irregular spacing of the aggregate of lines, be detected at a short distance from the head a gap in the general disposition of the lines which suggests that one line is missing at that point. This is the " centre " or " origin " of the band, and its position is of more real importance than that of the head, since it marks the true origin of the series of fine lines which compose the band.

The Fine Structure of the Individual Band.—The aggregate of lines within a simple electronic band can be provisionally divided into three series which we shall designate by α, β, and γ. The first of these is a sequence of lines with regularly increasing separation which proceeds from the centre towards the degraded end of the band. The second series β is a sequence which starts also from the centre and goes to the head of the band with regularly diminishing separation of consecutive lines. Actually the two series α and β may be regarded as forming a continuous sequence with one member of the sequence missing, namely, the missing line at their common origin. The third series of lines begins at the head of the band and goes towards the diffuse side with constantly increasing separation of consecutive lines. This series, however, may also be regarded simply as a *retrogressive* continuation of the β series, the separation of consecutive lines in the compound $\beta\gamma$ series first decreasing in the β branch, reaching a minimum at the head of the band, and then increasing again in the retrograde branch. In agreement with the essential continuity of all three series, the frequencies of all the lines in the band are mathematically represented to a close approximation by a single formula, of the type

$$\nu = a_1 + b_1 m + c_1 m^2 \quad . \quad . \quad . \quad (23)$$
$$(m = \pm 1, \pm 2, \pm 3 \ldots)$$

The frequency $\nu = a_1$ gives that of the missing line at the centre of the band. The constant b_1 is always positive, c_1 however, may be positive or negative. The arrangement of lines within a simple electronic band according to the above formula is best seen by plotting ν as abscissa against m as ordinate and taking the projections of whole number ordinates—positive and negative—upon the abscissa axis. The pattern which results for $-^{ve}$ values of the constant c_1 is shown in Fig. 8, and this is the actual appearance which the completely resolved band would present. All bands which degrade towards the red have a negative value of c_1, and the head of the band is contained in the positive branch of the parabola, i.e. m positive. For positive values of c_1, on the other hand, the band degrades towards the violet, and the head occurs in the negative branch of the parabola. The three series α, β, and γ discussed above are made up of the lines obtained from the projections of sections *NA*, *AL*, and *LM* respectively. A more natural division of the totality of lines into *two* series, however, is suggested by the fact that the parabola naturally divides itself into two branches which correspond to positive and negative values of m. The two series

$$\left.\begin{aligned} \nu &= a_1 + b_1 m + c_1 m^2 \\ \nu &= a_1 - b_1 m + c_1 m^2 \end{aligned}\right\} \qquad (m = 1, 2, 3, 4 \ldots) \qquad (24)$$

are referred to as the R or positive branch and the P or negative

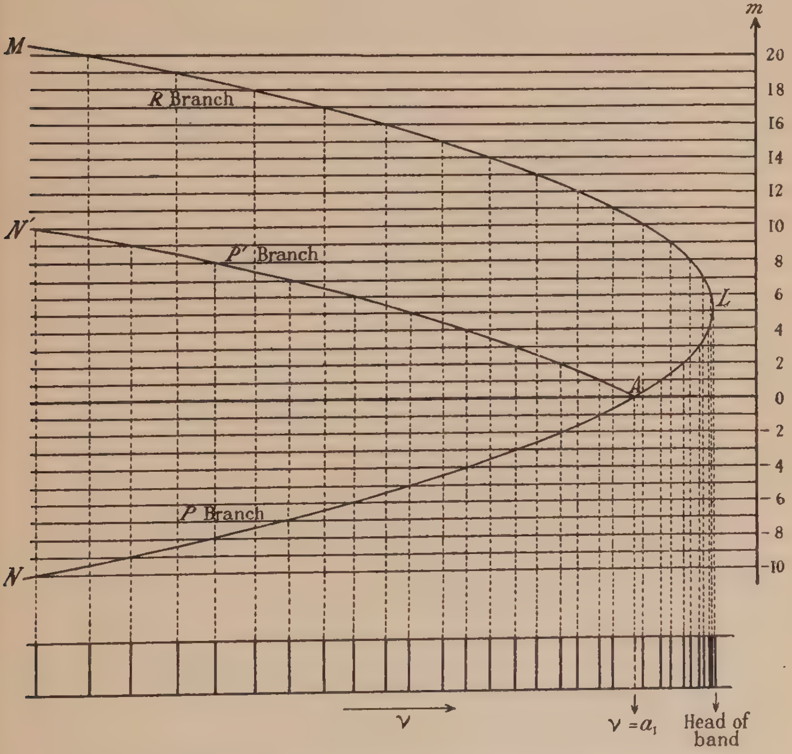


FIG. 8.—Resolved electronic band which degrades towards the red.

branch of the band respectively. The missing line at A separates the two branches from each other. A further justification for this division is found in the fact that the distribution of intensity in the lines of the two branches is roughly symmetrical with respect to the point A, the intensity rising fairly rapidly to a maximum on either side of A and then decreasing slowly. It should be mentioned that in the graphical representation of the lines as in Fig. 8 it is a convenient practice to plot both branches against positive values of m. This simply means that the P or negative branch is represented above the abscissa axis by P', the mirror image of the continuation of the R branch through A.

An interesting comparison may be made between electronic and near infra-red bands. These two types are apparently very different in their physical appearance, but actually they resemble one another to a marked degree in the details of their internal structure. Taking for comparison the infra-red absorption band of HCl shown in Fig. 7 and the simple two-branch electronic band of Fig. 8, we see that each consists of two series of lines starting out in opposite directions from a central missing line. The distribution of intensity is very similar for the corresponding branches of the two bands, the intensity first rising rapidly to a maximum and then falling slowly in either case. Again, the slight divergence and convergence of the left- and right-hand branches in the infra-red band find a qualitative analogue in the divergence of the electronic P branch and the convergence of the first members of the R branch respectively. It is in the retrogression or folding back of the R branch to form a band head that the analogy between the bands breaks down. The frequencies of the lines of both bands, however, conform to the same type of mathematical formula, and the superficial difference in their appearance is simply due to a difference in the relative magnitudes of the constants in the two expressions

$$\nu = \nu_v \pm bm + cm^2 \text{ (infra-red band)},$$

and

$$\nu = a_1 \pm b_1 m + c_1 m^2 \text{ (electronic band)}.$$

If we plot ν against m for negative values of c or c_1, the apex of the parabola, which fixes the head of the band, is reached when

$$m = -\frac{b}{c} \text{ or } -\frac{b_1}{c_1}.$$

For the infra-red band c is small compared with b, so that the theoretically possible head would only be attained for very high positive values of m, under which conditions the intensity of emission is zero. For the electronic band, however, b_1/c_1 is usually of such a value that the apex of the parabola is attained for small values of m, i.e. for lines whose intensity of emission is still very appreciable. Under these circumstances, a real band head is obtained.

The internal structure of most electronic bands is usually more complex than that so far dealt with. In many cases, besides the P and R branches of lines, the frequencies of which are included in the one series formula (23), there also exist lines belonging to a Q branch. The frequencies of the lines of this branch may in the simplest cases be represented by

$$\nu = a'_1 + c_1(m - \tfrac{1}{2})^2 \qquad (m = 1, 2, 3, 4 \ldots) \qquad . \quad . \quad . \quad (25)$$

The value of the constant a'_1 for this series of lines is very slightly different from that of a_1. The value of c_1 however, is the same in sign and in magnitude, so that the Q branch represents a divergent series of lines which always proceeds from the centre towards the shaded end of the band. It sometimes happens that the first line of the Q series occupies the position of the missing line of the P and R series, thereby making more difficult the practical identification of this point in the band, which is the common origin of all three branches.

A further complication arises from the fact that the individual members of the P, Q, and R branches are not necessarily single lines as hitherto implied. Actually, the great majority of electronic band systems are composed of doublets, triplets, or even higher multiplicities. Considering only doublet bands, these may, for practical purposes, be divided into two classes. In the first and simpler class, each band divides into two partial bands which in the frequency scale are exact duplicates of one another. The separation of the partial bands is usually fairly large, so that the two heads of the band do not interfere but are visibly separate and distinct. The spacing of the components of each double line is a constant independent of its serial number m, so that essentially each branch within the band splits up into two partial branches, both represented by the same formula $\nu = a_1 + b_1m + c_1m^2$, but with a different value of the constant a_1 for each. In double bands of the second class, matters are not so simple. Here the separation of the components of each doublet line may be approximately proportional to the serial number m of the line, or proportional to the square of m, or again the doublet separation may decrease as m increases, asymptotically approaching a constant value for large values of m. We need not enter further into these or the even more complicated structures of bands of higher multiplicity.

The Band Group or System.—So far we have discussed only the regularities which are to be found within each visible or ultra-violet band. The complete emission or absorption spectrum of a molecule, however, usually consists of a whole group of closely related bands or even of several such groups spread over a very extended spectral range through the visible and ultra-violet. Thus, in the band emission spectrum of nitrogen (un-ionised) there are at least three groups of bands, the so-called first, second, and fourth positive groups of nitrogen. The first positive group forms a system of some forty emission bands lying between 700 $\mu\mu$ and 500 $\mu\mu$, the second positive group another and independent system of nearly fifty bands between 530 $\mu\mu$ and 280 $\mu\mu$, the fourth positive group yet another system of bands lying in the extreme ultra-violet.

In many cases, the different systems of bands in the same spectrum overlap and this complicates the problem of their analysis. The first fact which helps to allocate the different bands to their proper systems is that bands which belong to one and the same system are very similar in the details of their internal structure. Again the bands which form a single group or system can usually be arranged into a number of regular series. These series can be chosen in three different ways. In some cases, the system of bands naturally divides itself up into several sub-groups or *sequences* which do not overlap. Thus the violet CN group of bands (cf. Fig. 9) form four separate *sequences* of bands which start from the positions 461 $\mu\mu$, 422 $\mu\mu$, 388 $\mu\mu$, and 359 $\mu\mu$ respectively. Within each of these sequences, the separation of successive band centres falls off progressively towards the violet, and the frequencies of the centres obviously conform to some simple mathematical law. Alternatively, however, all the bands in these four sequences can be ordered into a number of *Deslandres progressions*, each progression claiming one band from each of the four sequences. These Deslandres progressions can be chosen in two different ways.

In each *Deslandres first progression* of bands the members converge regularly from the violet to the red end of the spectrum, and the separations $\Delta\nu$ of the centres of successive members form a decreasing arithmetic progression in order of *decreasing* frequency. Otherwise expressed, the frequencies of the band centres within a first progression fit an equation of the type

$$\nu = \alpha' - \beta' p' + \gamma' p'^2 \quad . \quad . \quad . \quad . \quad (26)$$

where α', β', and γ' are positive constants and p' is a variable $+^{\text{ve}}$ whole number which is least for the band of greatest frequency. Only the constant α' changes from one first progression to another; in other words, the frequencies of the centres of the bands in one first progression may be obtained from those in another first progression simply by the addition of the same constant to each.

On the other hand, the bands in each *Deslandres second progression* converge regularly from the red to the violet, and the separations of successive bands form a decreasing arithmetic progression in the direction of *increasing* frequency. The frequencies of the band centres in a second progression are thus represented by

$$\nu = \alpha'' + \beta'' p'' - \gamma'' p''^2 \quad . \quad . \quad . \quad (27)$$

where again α'', β'', and γ'' are positive constants while p'' is a variable $+^{\text{ve}}$ whole number which is least for the band of lowest frequency in the progression. Moreover, only the constant α'' changes in passing from one second progression to another. Combining these facts, we see that the whole system of bands contained in the four sequences can be represented by a quadratic function of two independent parameters p' and p'', viz.

$$\nu = \nu_0 - \beta' p' + \beta'' p'' + \gamma' p'^2 - \gamma'' p''^2 \quad . \quad . \quad (28)$$

In each first progression p' varies and p'' remains constant; in each second progression p'' varies and p' remains constant. The sequences themselves are formed by bands for which p' and p'' simultaneously vary, but $(p'' - p')$ remains constant. Different sequences correspond to different constant values of $(p'' - p')$. In Fig. 9 are shown the four sequences which form the violet CN group of bands. Below these, the bands which form the various first progressions are picked out and arranged in horizontal series. The diagonal dotted line links up the bands of a representative second progression.

Not in all band systems are the sequences into which the band heads or centres fall as obvious as in the case just dealt with. In the first positive group of nitrogen, the sequences are much longer than in the violet CN group and they overlap considerably. In the second positive group of nitrogen (cf. Fig. 28, p. 198), the separate sequences stand out clearly only in the farther ultra-violet portion of the spectrum. Nevertheless, in these and in numerous other cases it is always possible to resolve the confused medley of bands into sequences, first progressions, and second progressions, and to show that the totality of bands within each system conform as regards the frequencies of their centres to a two-variable function of the same type as (28). Writing this relation in the general form

$$\nu = f''(p'') - f'(p') \quad . \quad . \quad . \quad . \quad (29)$$

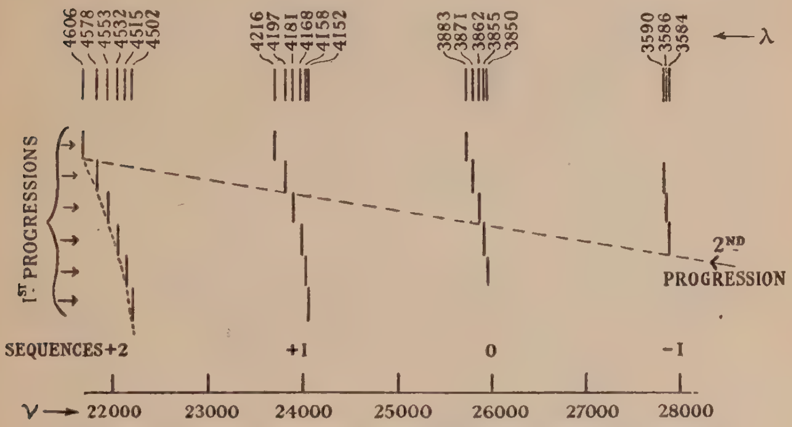


FIG. 9.—The violet cyanogen group of bands arranged in Deslandres progressions.

makes clear at once the applicability to band systems of the Ritz Combination Principle already dealt with in connection with line series spectra. The frequency of each band in a system can be expressed as the difference of two terms, and with certain reservations each difference of terms gives the frequency of an observed band. Further, each combination term is once again expressed as a function of a variable positive whole number, although in the case of the terms of a band system the nature of the function is very different from that of the Rydberg function which features in the line spectra of atoms.

Following from equation (29), the building up of sequences and progressions in a band system can be represented schematically as in Fig. 10. Here the values of the terms $f'(p')$ and $f''(p'')$ for various values of p' and p'' are represented by the heights of the horizontal levels above an arbitrary zero level. The difference between any $f''(p'')$ level and any $f'(p')$ level gives the frequency of an observed band. The series (a) and (a') are representative first progressions with

p'' constant and p' variable in each. The series (b) is a second progression with p' constant and p'' variable. The series (c) gives a sequence of bands for which $(p'' - p')$ is a constant. On the same diagram it is possible to illustrate the general relationship of near infra-red absorption bands to the electronic emission bands of the same substance. Referring back to the near infra-red absorption spectrum of hydrochloric acid, it will be seen that this consists of three bands, a fundamental and a first and second harmonic, the frequencies of whose centres stand approximately in the ratio 1 : 2 : 3.

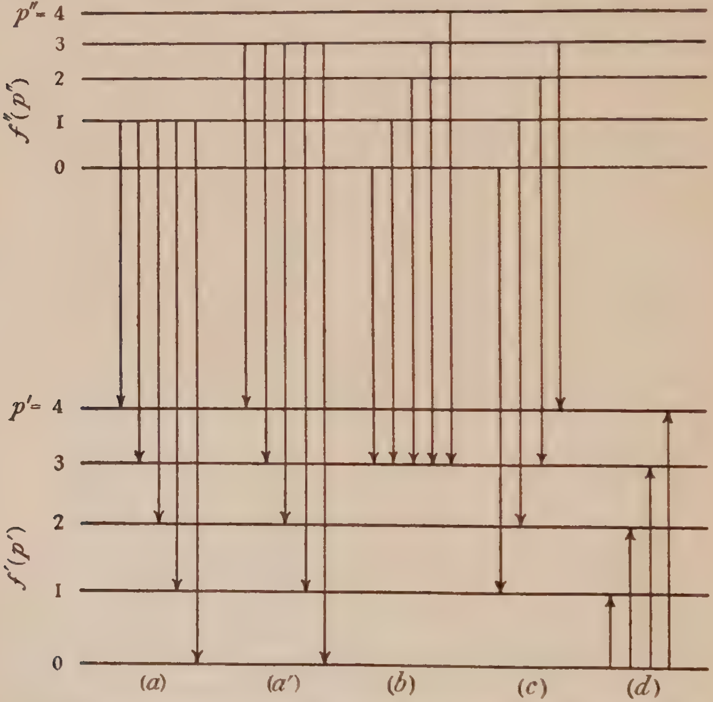


FIG. 10.—Vibrational sub-levels of molecule in two states of electronic excitation.

These bands really form a system in the near infra-red, and this system is represented by (d) in the diagram. The system may be regarded as a special type of Deslandres second progression within the $f'(p')$ group of levels. In terms of the modern theory of the origin of spectra, the various term levels in Fig. 10 correspond to different internal energy contents of the emitting or absorbing molecule. The $f'(p')$ levels may represent the various amounts of vibrational energy which the molecule can possess without simultaneous electronic excitation. The higher $f''(p'')$ levels would then correspond to the various successive states of vibrational energy content which accompany an electronic excitation within the molecule. From any one of the $f''(p'')$ levels to any one of the lower $f'(p')$ levels the excited molecule can pass with emission of radiation of a frequency proportional to the amount of energy lost. Such transitions give rise to the various bands of a system in the visible or ultra-violet band emission spectrum, and the fine structure of each band owes its origin to the variable amounts of rotational energy which may be associated with the molecule in its initial and in its final state. On the other hand, the molecule in its normal non-vibrating state, with energy content corresponding to the level $f'(0)$ can, by absorption, either change its vibrational energy alone giving rise to an absorption band in the infra-red system (d), or change its vibrational and electronic energy contents simultaneously with absorption of one of the bands in the visible or ultra-violet systems.

Different Band Groups.—While the multiplicity of bands within one and the same system is referred to the variable amount of vibrational energy which can be associated both with the initial and with the end condition of the emitting molecule, different systems or groups of bands in the electronic emission spectrum of a molecule arise from the existence of more than one possible state of electronic excitation. To illustrate this, the diagram of Fig. 10 could be extended upwards by the introduction of higher electronic levels $f'''(p''')$, $f''''(p'''')$, etc., within each of which is a series of concomitant vibrational levels. The Principle of Combination applies equally to the terms of these higher electronic levels. Thus the positions of all the bands in the first, second, and fourth positive groups of nitrogen can be built up as differences of four series of terms, viz.

1st positive group : $\nu = f''(p'') - f'(p')$
2nd ,, ,, : $\nu = f'''(p''') - f''(p'')$
4th ,, ,, : $\nu = f''''(p'''') - f''(p'')$.

The origin of a band system is the position of that band, whether observed or calculated, for which the two parameters of the system p' and p'' are both zero. The emission of this band involves only an electronic disturbance in the vibrationless molecule. Hence the terms $f'(0)$, $f''(0)$, $f'''(0)$, etc., which combine to give the frequencies of the origins of the various band systems in a complete band spectrum, characterise the various electronic energy levels of the molecule in the same way as the terms from which the series spectrum of an atom are built up characterise the various electronic energy levels of the atom. It should be anticipated, therefore, that systemisation of the $f'(0)$, $f''(0)$, $f'''(0)$, etc. terms in molecular spectra should be possible along the lines already developed in the case of atomic spectra. Work in this direction is now in progress. It is unnecessary to enter into details since this branch of investigation is still in its infancy, but we may remark that there already appears to be a very close parallelism between the characteristics—multiplicity, combining possibilities, etc.—of the electronic spectral terms of molecules and the optical terms of atoms.

CHAPTER II.

QUANTUM THEORY AND ATOMIC STRUCTURE.

TEMPERATURE RADIATION.

The general term "luminescence" is used to embrace all the types of emission of radiant energy referred to on page 7 with the exception of that due to thermal excitation alone. Pure temperature radiation is emitted by a substance when its physical and chemical condition depends upon the single variable—temperature. The possibility of physical or chemical changes taking place in the radiating system is not excluded, but such changes, if they occur, must be balanced changes, that is, the system must be in a state of dynamical equilibrium. The emission of temperature radiation is continuous and constant with time provided the temperature of the body is maintained steady by the supply of heat from outside. On the other hand, the various phenomena of luminescence are not uniquely determined by the physical and chemical nature of the radiating substance and by its temperature, but are dependent also on its previous history, or on the action of electric fields, or on bombardment with ions or electrons, or on the occurrence of unbalanced chemical changes in the system. In the absence of external illumination, electrical excitation, directed chemical action, etc., the luminescence ceases in time even when the temperature is maintained constant.

The intensity and the spectral characteristics of the temperature radiation emitted by any body depend upon its physical and chemical properties and upon the absolute temperature. The gross intensity of emission always increases as the temperature increases, and simultaneously the spectral distribution of the radiant energy changes in such a way that the emission of the shorter wave-lengths becomes relatively stronger the higher the temperature. The thermal radiation of solids and liquids at any temperature usually presents a continuous spectrum, that is, the emission contains rays of every possible wave-length. However, in the spectral regions where the substance possesses selective absorption, there may also be a selective emission which may take the extreme form of a line or band spectrum superimposed upon a continuous, luminous background. Most solids and liquids emit visible light in appreciable intensity when their temperature is raised to about 500° to 700° C. Matter in the vapour or gaseous state is comparatively non-luminous, but it would be incorrect to say that any gas or vapour is completely so, though in certain cases (such as nitrogen, oxygen, and the rare gases) the highest temperatures available in the laboratory do not suffice to induce any measurable temperature emission. The vapours of the metals and of certain of their salts give an appreciable temperature emission at comparatively low flame temperatures, and a true temperature emission is experimentally observed with most metal vapours by heating in an electric oven to 2000° or 3000° C. The "furnace" spectrum thus produced is a series line spectrum, essentially similar in character to the spectrum of the metal which is developed in the hot Bunsen flame or in the electric arc, spark, or discharge. As the furnace temperature increases, the higher (shorter wave-length) members of the series spectrum are successively developed in the emission of the vapour. The Bunsen flame spectra of the metals are often quoted as examples of chemiluminescence rather than of pure temperature emission; but while the emission from the so-called cold flames certainly belongs to this category, it is probable that in the normal Bunsen flame, fed with a metal or the salt of a metal, the bulk if not all of the emission observed is a pure temperature emission. The increased luminosity as compared with that of the salt- (or metal-) free flame is due to the fact that in the former case the high temperature zone is enriched with atoms which respond readily, compared with the products of combustion CO, CO_2, and H_2O, to thermal excitation. The chemical process of combustion in the Bunsen flame serves to maintain the high temperature required for the thermal excitation of the metal atoms.

In the temperature radiation of solids, which has been most extensively studied, the optical condition of the radiating surface plays a specially important part, since the intensity of emission at any temperature is to a large extent determined by the roughness or smoothness of the radiating surface relative to the various wave-lengths in the emission spectrum. Thus, while the polished surface of a hot metal is a poor radiator of visible light, roughening of the surface increases very markedly its intrinsic brightness for the same temperature. As we shall see immediately, this result is intimately related to the fact that the polished metal surface is also a good reflector for visible light. A hypothetical body with a perfect reflecting surface could emit no radiation whatsoever, since otherwise the energy content of the body would progressively diminish and its temperature fall to the absolute zero, if it were placed in a uniform temperature enclosure but out of direct *physical* contact with any other material bodies in the enclosure.

Absorptive Power of Substances.—When a beam of monochromatic radiation falls on a surface of discontinuity, any or all of three effects occur—reflection, transmission, and absorption. In the case of incidence on a smooth surface, some reflection of the radiation must always take place, the greater in amount the greater the angle of incidence of the beam. Complete passage across the surface separating two media is in fact only possible when their refractive indices for the radiation in question are identical. The greater the difference in the two refractive indices, the larger is the fraction of the radiation which is reflected at the bounding surface. For perpendicular incidence the fraction reflected is given by $\left(\frac{n-1}{n+1}\right)^2$, where n is the refractive index of the second medium relative to that of the first.

That part of the beam which actually penetrates the surface will be transmitted through the second medium without further loss in intensity if this second medium is perfectly transparent to the radiation in the beam, otherwise either scattering or true absorption of the radiation takes place. Now the absorptive power A of a substance is defined as the ratio of the radiant energy absorbed by it to the energy radiated upon it from without. By this definition, A is clearly a function, not only of the frequency of the incident radiation and of the physical properties and dimensions of the body, but also of the optical conditions at the surface of incidence of the radiation. The absorptive power of a given body for radiation of a definite frequency depends upon the refractive index of the contiguous medium, since this governs the fraction of the incident radiation which is lost by reflection. Since there is always some reflection at the surface unless the refractive index of the body is identical with that of the surrounding medium, A is in general less than the fraction of the penetrating radiant energy which is actually absorbed and which would correspond to the true absorption coefficient of the body. For example, the absorptive power A for visible radiation of a metal with highly polished surface and surrounded by air is very much less than the true extent of absorption of radiation by the metal, since practically all incident light is reflected at the polished surface.

A perfectly *black surface* would be one permitting all radiations to penetrate it without reflection, whether direct or diffuse. A perfectly *black body* is one for which A is unity, that is, it has the property of allowing all incident radiation to enter it without surface reflection and of not allowing it to leave again. Obviously, a perfectly black body must, in the first place, have a black surface for radiation of all frequencies; in the second place, it must have a minimum thickness, determined by the true absorption coefficients of its substance for radiation of all frequencies. The direct experimental realisation of a perfectly black body is, therefore, a physical impossibility. Substances which are more or less black with respect to restricted ranges of frequency are, however, available, e.g. lamp black and platinum black act as such for visible light. In these cases, the first condition of surface blackness is apparently not fulfilled since there is a discontinuity of refractive index in passing from air or from a vacuum to the "black" body. Regular reflection of the incident radiation is, however, avoided by virtue of the rough porous nature of the surface which acts as a light trap. Each incident ray suffers not one but a very large number of successive reflections before it can leave the surface, and each reflection reduces the intensity of the reflected ray so that the final emergent intensity is zero. The efficacy of this action is conditioned by the degree of roughness of the surface being comparable with the wave-length of the incident radiation. A surface of platinum black which is efficient in absorbing visible light would not, of course, act equally well in absorbing radiation of much longer wave-lengths, to which the surface would be relatively smooth. An indirect method of realising conditions which reproduce the ideal black surface and black body as defined above will be indicated below.

Kirchhoff's Law and Equilibrium Radiation.—It is a matter of observation that a qualitative correspondence exists between the radiating and absorptive powers of substances for temperature radiation. Bodies which possess a large radiating power also exhibit strong absorption for the same type of radiation, while those which are practically transparent to some part of the spectrum emit but feebly within the same spectral limits. That it is not the true absorptive capacity but the absorptive power of a substance, as defined above, to which its radiating power is related is indicated by the fact that, although a metal—say platinum—has a very large true absorptive capacity for visible light, the polished metal has a low absorptive power and a correspondingly low radiating power, whereas roughening of the surface increases both of these to a marked extent. All these facts receive quantitative expression in *Kirchhoff's Law* which states that the ratio between the radiating and absorptive powers of any substance for temperature radiation is a function of the temperature only and is independent of the nature of the substance or of the optical condition of its surface. Since in general the specific intensity of emission K from any surface depends upon the angle of emission (cf. p. 11), the absorptive power A in the Kirchhoff relation $\frac{K}{A} =$ constant must naturally refer to the same angle of incidence of the impinging beam of radiation as that angle of emission which determines K. In the case of a perfectly black body, the absorptive power is—by definition—equal to unity for all angles of incidence; hence the intensity of emission K of a perfectly black body is independent of the orientation of the emitted radiation to the surface, and is a function of the temperature only. Also, in virtue of its maximum absorptive power, the value of K for a black body at any temperature represents the maximum possible intensity of emission (of pure temperature radiation) of any substance whatsoever at this temperature.

Kirchhoff's Law applies not only to the total temperature emission, but also to the emission in each separate frequency interval in the complete spectrum. Accordingly K_ν, the specific intensity of emission of radiation of frequency ν for any substance, must always be less than the corresponding quantity in the emission of a perfectly black body at the same temperature, being in fact equal to K_ν for the black body multiplied by the absorptive power of the substance for the frequency ν. The specific intensity of emission K_ν of the black body must be a function of ν and T only; the value of K_ν for the non-black body, however, is also determined by its physical properties and by the optical condition of its surface.

The following simple derivation of Kirchhoff's Law, although by no means rigid, will serve to introduce the concept of "equilibrium radiation" and to show the essential identity of this with black body radiation. Consider a system comprising a vacuous enclosure surrounded on the outside by perfectly reflecting walls, and containing various substances a, b, c . . . One of these substances a we will assume to be a perfectly black body. Whatever the initial state may be, the system will, in the course of time, attain a condition of equilibrium characterised by temperature equality throughout the enclosure. The latter will then be permeated by a homogeneous field of radiation which is termed the "equilibrium radiation" for the steady temperature concerned. Any imaginary surface element in the interior of the enclosure transmits radiation through it of equal intensity in opposite directions, and when we speak of the specific intensity of the homogeneous radiation field we mean thereby the specific intensity of any such imaginary element of surface in the interior, defined in exactly the same way as the specific intensity of emission of a material surface would be (cf. p. 13).

Under the conditions of equilibrium, each of the substances a, b, c . . . must send out into the adjacent space as much radiant energy as it receives from this space. At the surface of b, for example, the energy interchanges for any particular frequency ν are as follows :—

(1) radiation incident on the surface from without $\propto K_\nu^f$, where K_ν^f denotes the specific intensity of the field for the frequency ν;

(2) reflection (and transmission) by the surface $\propto K_\nu^f\,(1 - A_\nu^b)$, where A_ν^b is the absorptive power of b for radiation of the frequency ν;

(3) emission by b into the adjacent space $\propto K_\nu^b$, where K_ν^b is the specific intensity of emission of b for the frequency ν.

For temperature equilibrium (1) must balance (2) and (3), and therefore

$$K_\nu^f = K_\nu^f(1 - A_\nu^b) + K_\nu^b,$$

that is

$$\frac{K_\nu^b}{A_\nu^b} = K_\nu^f.$$

Exactly the same relation must hold for all frequencies and for all other material substances a, c, d . . . in the enclosure. Hence the ratio $\frac{K_\nu}{A_\nu}$ is independent of the nature of the substance, which is Kirchhoff's Law. In particular, for the black body $\frac{K_\nu^a}{A_\nu^a} = K_\nu^f$, and since A_ν^a is by definition equal to unity for all frequencies, hence $K_\nu^a = K_\nu^f$

over the whole spectrum. The radiation emitted by a perfectly black body is therefore identical with the equilibrium radiation in a uniform temperature enclosure.

We see then that while the temperature radiation which is emitted by any arbitrary substance is not amenable to thermodynamic treatment, since it depends not only upon the nature of the substance but also upon such non-thermodynamic variables as the optical condition of the surface, the emission of a black body can so be dealt with, since its properties are simply those of radiation in thermodynamic equilibrium with matter. The identity of black body and equilibrium radiation leads to the following simple, if indirect, method of realisation of the former for the purpose of experimental examination of its properties.

The radiation contained in a uniformly heated enclosure with blackened walls (a "hohlraum") is the equilibrium radiation corresponding to the temperature of the enclosure, provided that, for every frequency in the complete spectrum, the enclosure contains some matter which is not transparent to that frequency. This condition is fulfilled by coating the walls with lamp black which by absorption and emission of all frequencies will change any arbitrary state of the radiation initially present in the enclosure to that state characteristic of temperature equilibrium. The emission from a small orifice in the side of the enclosure will then possess all the properties of equilibrium radiation, that is, it will be identical with the emission from the surface of a perfectly black body. It was by such an arrangement as this that Lummer and co-workers studied experimentally the properties of black body radiation, verified the predictions of thermodynamics contained in the Stefan-Boltzmann Law and Wien's Displacement Law, and indicated the actual dependence of the intensity K_ν upon ν and T which was later interpreted by Planck in terms of the Quantum Theory.

The Stefan-Boltzmann Law and Wien's Displacement Law.—The Stefan-Boltzmann Law, first suggested on experimental grounds by Stefan, and afterwards given a thermodynamic basis by Boltzmann, states that the total intensity of emission of a black body is proportional to the fourth power of its absolute temperature; thus

$$K = \sigma T^4 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ is a universal constant. This relation within the last thirty years has been subjected to repeated and rigorous experimental test, and has been amply verified over a large range of temperature. The best representative value of the constant σ, which is left undetermined in the thermodynamic deduction, is $1{\cdot}82 \times 10^{-5}$ in absolute c.g.s. units. The law can be alternatively stated in the form: $u = a \,.\, T^4$, where u is the volume density of equilibrium radiation and a is a constant. The values of u and a are both $4\pi/c$ times the values of K and σ respectively, c being the velocity of light *in vacuo*.

While Stefan's Law gives the total energy of the complete emission spectrum of a black body, Wien's Displacement Law is concerned with the distribution of this total energy over the spectrum. The law, which is derived by a combination of thermodynamic considerations with the Doppler principle, states that K_ν must depend on ν and T according to a relation of the type

$$K_\nu = \nu^3 . F\left(\frac{\nu}{T}\right) \quad . \quad . \quad . \quad . \quad (2)$$

where $F(\nu/T)$ is an undetermined universal function of the quotient ν/T. Although verified experimentally in the form of its two corollaries

$$\nu_m \propto T \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$K_{\nu_m} \propto T^3 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where ν_m is the frequency for which K_ν is a maximum, the first form best indicates how far the Displacement Law falls short of a complete solution of the radiation problem. The nature of the universal function F remains to be determined, and in this matter thermodynamic reasoning alone offers no further help.

THE ORIGINS OF THE QUANTUM THEORY.

Black-Body Radiation Formulæ.—To obtain the complete expression of K_ν in terms of ν and T, it is necessary to be more explicit than pure thermodynamic analysis requires regarding the nature and operation of the ultimate processes by which radiant energy is produced and destroyed by matter. It would at first sight appear that any attempt to relate our imperfect knowledge of these processes to the conditions obtaining in a hohlraum should be doomed to failure, since the maintenance of equilibrium between any actual matter and the radiation field in a temperature enclosure must involve an exceedingly complex history of any arbitrarily chosen wave train of radiation or of any arbitrarily chosen system of material units therein. However, the analysis is to some extent simplified by two facts. In the first place, just because we are dealing with equilibrium conditions, we are permitted to idealise the matter in the hohlraum. We can use the simplest possible material model which, according to electrodynamic principles, is capable of generating and absorbing radiation, and we then know that when a system of such models in a hohlraum is in equilibrium with radiation of such frequencies as they can absorb and emit, *that* radiation must possess all the characteristics of black body radiation of the same quality. In the second place, the condition of thermodynamic equilibrium introduces a further simplification by permitting the application of statistical methods of analysis to the problem.

The first attempt to deduce the complete expression for K_ν of black body radiation along these lines was made by Wien. As the material system in equilibrium with black body radiation, Wien used an assembly of gas molecules free to move about in the temperature enclosure and with their linear velocities distributed in accordance with Maxwell's Distribution Law. He further assumed that radiation is emitted and absorbed by the molecules in terms of a special coupling between the velocity of a molecule and the frequency of radiation with which it can interact. On this basis he obtained for the intensity K_ν of black body radiation of frequency ν the expression

$$K_\nu = \alpha\nu^3 e^{-\beta\nu/T} \quad . \quad . \quad . \quad . \quad (5)$$

where α and β are undetermined constants. This equation is in formal agreement with Stefan's Law and also with Wien's Displacement Law and its corollaries. Moreover, it reproduces, with suitably chosen values for α and β, the observed variation of K_ν with ν and with T for high values of the quotient $\beta\nu/T$. For small values of $\beta\nu/T$, however, K_ν does not fall off nearly so rapidly as the equation predicts.

A radiation formula which rests upon a much sounder *theoretical* basis than the above is that usually associated with the names of Rayleigh and Jeans. This takes the form

$$K_\nu = \frac{\nu^2}{c^2} . kT \quad . \quad . \quad . \quad . \quad (6)$$

where k is the gas constant per molecule. The deduction of this equation depends upon a combination of the results of classical electrodynamics and statistical mechanics. The material model chosen is a simple electrical dipole fixed in space but capable of executing linear harmonic vibrations of frequency ν, so that, according to classical theory, there is a continuous exchange of energy between the model and a radiation field of the same frequency. A system comprising a large number of such oscillators will be in equilibrium with such a radiation field if the specific intensity of frequency ν of the field is given by

$$K_\nu = \frac{\nu^2}{c^2} . \bar{U} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In this relation $\bar{U}$ is the average energy of vibration of an oscillator for thermodynamic equilibrium of the system. The value of $\bar{U}$ as obtained from classical statistical mechanics is

$$\bar{U} = kT \quad . \quad . \quad . \quad . \quad . \quad (8)$$

so that the Rayleigh-Jeans formula follows.

Exactly the same expression for K_ν is derived if material models more complex in character than the simple linear oscillator are employed in the analysis.*

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* Cf. Jeans, *Report on Radiation and the Quantum Theory*, 2nd edition, 1924.

The Rayleigh-Jeans equation is consistent with Wien's Displacement Law in its functional form

$$K_\nu = \nu^3 . F\left(\frac{\nu}{T}\right),$$

but not with the above-mentioned corollaries to this law. These corollaries are derived on the assumption that K_ν becomes zero both for very low and for very high frequencies, so that the plot of K_ν against ν should always exhibit a maximum for some value of the frequency. Whilst this is actually the case, the Rayleigh-Jeans equation, however, predicts that K_ν should increase indefinitely with increasing frequency. We see at once, therefore, that the formula cannot express the observed variation of K_ν with ν over the complete spectrum. It is found, however, that while Wien's radiation formula holds for *large* values of ν/T, the equation of Rayleigh and Jeans reproduces the experimental data very faithfully if we restrict ourselves to *small* values of this same quotient. Each of the two equations has a limited range of applicability.

We therefore possess three criteria with which a satisfactory law of black body radiation must comply :—

(1) It should be consistent with Wien's Displacement Law and its corollaries.
(2) It should degenerate to Wien's radiation formula in the limit of large values of ν/T.
(3) It should yield the Rayleigh-Jeans radiation formula as a limit for small values of ν/T.

All these conditions are fulfilled by Planck's Law of black body radiation which expresses K_ν in the form

$$K_\nu = \frac{h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1} \quad . \quad . \quad . \quad . \quad (9)$$

In this, h is a universal constant having the physical dimensions of action (energy × time) and the value

$$h = 6{\cdot}55 \times 10^{-27} \text{ erg-sec.}$$

Before we discuss the assumptions underlying Planck's derivation of this radiation formula, we may briefly refer to the question of its range of applicability. The early work of Rubens and Kurlbaum, Paschen, and Warburg and co-workers in Germany appeared to confirm the relation in all essentials over wide spectral and temperature limits. Later, Nernst and Wulf from a critical survey of these data have concluded that, in the spectral region lying between the limits of applicability of Wien's formula and of that of Rayleigh and Jeans, Planck's equation also does not strictly apply, deviations up to about 7 per cent. being claimed. Rubens and Michel, however, have re-examined this spectral region (between 4 μ and 52 μ) with variation of the black body temperature up to 1500° C., and find that the conclusions of Nernst and Wulf cannot be substantiated. For all their observations, Planck's formula holds to within 1 per cent. Regarded solely from the empirical standpoint, the equation is, therefore, by far the most satisfactory which has yet been proposed.

The Quantum of Energy.—In deriving his equation Planck (1900) found it necessary to make a serious departure from the then orthodox views regarding the mutual interaction of radiation and matter. Comparing equation (9) with (7) we see that if the latter equation expresses correctly the relation between K_ν and $\bar{U}$, then $\bar{U}$ cannot have the value kT prescribed by classical statistical mechanics, but must be given by

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad . \quad . \quad . \quad . \quad (10)$$

It may be shown, however, that this is the average energy per oscillator which would be obtained for a system of oscillators, the energy content of each of which could not assume an infinite continuum of values, but only the discrete values 0, $h\nu$, $2h\nu$, $3h\nu$ . . . It appears, then, that these and these only should represent the possible energy levels of the linear simple harmonic oscillator, and therefore that the exchange of energy between an oscillator and a radiation field should take place, not continuously as demanded by classical electrodynamics, but as discontinuous events. Each such event would involve the transformation of a finite quantity of mechanical energy of vibration of the oscillator, in amount equal to $h\nu$, into radiant energy, or *vice versa*. The unit of energy $h\nu$ which appears here is called a *quantum of energy*. Its value, however, is not a universal constant as is h itself, but is proportional to the frequency of the radiation or that of the oscillator with which it is associated.

The concept of discrete energy exchanges between matter and radiation, whilst entirely foreign to classical electrodynamics, has played a most important part in the development of modern atomistics. We need not discuss here Planck's subsequent attempts to effect a partial reconciliation between the classical and quantum views by the assumption that these discrete energy exchanges take place only in the emission of radiation, that is, in the event of *loss* of energy by a material oscillator. Neither need we dwell on the inconsistency inherent in his first deduction of the black body radiation formula which involves a violation of classical principles in the matter of the value ascribed to $\bar{U}$, but at the same time retains one result of the classical electrodynamics in equation (7). A more self-consistent, if at the same time more formal, derivation of the black body radiation formula has been given by Einstein and will be discussed in Chapter III.

The Photoelectric Effect and Light Quanta.—The trend of physical discovery during the last twenty years has been in the direction of confirming in its essentials Planck's original conception that energy exchanges take place in quanta, both for the emission and for the absorption of radiation by matter. The remarkable fertility of the principle was first realised following upon Einstein's application (1907) of Planck's equation (10) for the average energy content of a linear oscillator to the problem of the variation of the specific heats of solids with temperature. Previous to this, however, independent support of the quantum theory had been obtained by Einstein's interpretation of the photoelectric effect. When ultra-violet (and in some cases, visible) radiation falls upon a clean metal surface, the surface acquires a positive charge due to an emission from it of "photoelectrons." The production of secondary cathode rays (high speed electrons) by the action of X-rays on a metal surface is essentially the same phenomenon. The chief characteristics of this photoelectric effect are (1) the number of photoelectrons liberated per second from a given surface by illumination is directly proportional to the intensity of the radiation used; (2) the maximum velocity with which the photoelectrons are ejected depends, not upon the intensity of the radiation, but only upon its frequency, and this maximum velocity increases progressively as the frequency of the radiation used is increased; (3) for each metal there is a definite threshold frequency ν_0 below which no photoelectrons are liberated from the surface, however great the intensity of the incident radiation may be.

These results of observation, which are very difficult to account for on classical views, receive a surprisingly simple explanation in terms of an equation first suggested by Einstein, viz.

$$\tfrac{1}{2}mv^2 + W_0 = h\nu \quad . \quad . \quad . \quad . \quad (11)$$

This relation signifies that a quantum of radiant energy of the effective frequency ν is transferred to an electron which is loosely bound or free in the metal surface. A part W_0 of this transferred energy is required to free the electron from its binding and to carry it through the surface, the remainder appears as the energy of free translatory motion $\tfrac{1}{2}mv^2$ of the liberated electron. The threshold frequency ν_0 is given by the condition that the velocity v of ejection of the photoelectrons should be zero, and accordingly ν_0 is equal to W_0/h.

Equation (11) has been tested experimentally for a large number of metals, and is found to express quantitatively the observed relationship between v and ν. It has been used by Millikan in what constitutes the most direct and at the same time one of the most accurate methods for the determination of the numerical value of the Planck constant h. For a given metal surface, the values of the maximum kinetic energy of the liberated electrons were measured for a number of photoelectrically active frequencies. The numerical value of h is then given by the slope of the straight line obtained by plotting this kinetic energy against the frequency.

In proposing a quantum theory of the energy exchanges between a system of linear oscillators and the surrounding radiation field, Planck considered that the discontinuous nature of these processes should be laid entirely to the account of the material oscillator in the sense that the energy content of the latter could only be a simple multiple of an energy unit $\epsilon = h\nu$, characteristic of the oscillator. He sought to retain the classical view that the radiation field itself is undulatory, continuous, and capable of description in terms of Maxwell's electromagnetic equations. Einstein, however, preferred the view that the quantum discontinuity is primarily a characteristic of the radiation itself. On this extreme view, the Planck oscillator which absorbs and emits radiation of frequency ν assumes the discrete energy levels $E = nh\nu$ ($n = 0, 1, 2, 3 \ldots$) by virtue of the fact that the radiation is itself discrete and quantised. Thus a radiation field of frequency ν is supposed to consist of a number of quanta of radiant energy—light quants—each of magnitude $h\nu$, and each propagated through space with the velocity of light.

Certain aspects of the photoelectric effect are more readily explicable as a direct transformation of the energy of such a light quant into kinetic energy of the ejected electron. The continuous field hypothesis requires that the photoelectrons liberated by light of frequency ν should be those originally capable of vibration about equilibrium positions in the metal with this same frequency, these electrons being liberated as a result of the violent sympathetic vibrations induced in them by the electric vector of the incident radiation. The intensity of the incident beam should on this basis govern not only the number of photoelectrons set free but also the velocity with which they are set free. According to the light quant view, however, the intensity of the radiation is only a measure of the number of light quants incident on the metal surface and should therefore determine the number of photoelectrons ejected, but not their velocity. Again, the classical view requires that the radiant energy in the incident beam should be distributed uniformly over the whole wave front, and the liberation of photoelectrons should therefore exhibit a time lag, equal to the time required for the incident train of waves to pass sufficient energy through the cross-section of the sphere of influence of the photoelectron to effect its liberation. No such lag is observed, however, even with the weakest intensities of illumination, and it is not to be anticipated if we assume that the radiant energy is not uniformly distributed over the whole wave front, but is concentrated in " bundles " only at certain points in the incident beam.

The extreme light quant theory receives additional support from the phenomena attending the interaction of X-rays with matter. When a beam of X-rays which, according to classical views, should present a continuous wave front, impinges upon a metal surface, secondary cathode rays (electrons) are immediately liberated, however weak be the intensity of the X-ray beam. Again when X-rays are absorbed by a gas which they ionise, the incident beam does not react uniformly upon all the molecules which lie within its cross-section, but only a small proportion of these are ionised. Each of these molecules appears to draw the energy necessary for its ionisation from a section of the wave front of the radiation which is very great compared with the cross-section of the molecule itself. These phenomena again seem to require the existence of concentrated units of radiant energy in the incident beam for their interpretation.

The same is also true for the *Compton Effect*—the name given to the change (decrease) in frequency which accompanies the diffuse scattering of X-rays or γ-rays by matter. This scattering is quite a different effect from the production of secondary X-rays by a primary beam of X-rays. The latter is a kind of fluorescence, and the frequency of the secondary X-rays is normally quite different from that of the primary X-ray which excites it, and is a characteristic of the absorbing medium. The phenomenon known as the Compton Effect, however, is the analogue of the Tyndall scattering of light in the visible region of the spectrum, although in the Tyndall Effect there is apparently no frequency difference between the primary and the scattered radiation such as is met with in the case of X-rays and γ-rays. In the Compton Effect this change in frequency of the scattered X-ray is a function of the angle of scattering, but it is normally quite independent of the nature of the scattering medium. A hard X-ray line is, for example, found to suffer exactly the same change in frequency when scattered in such very different media as the alkali metals, carbon, hydrogen, oxygen, and sodium chloride.

In the classical theory of the scattering of X-rays, developed by J. J. Thomson, the phenomenon is ascribed to the forced vibrations which will be excited in free or loosely bound electrons in the medium by the alternating electric vector of the primary X-ray pulse, these electrons becoming secondary centres for the emission of the scattered radiation. Thomson's theory, whilst it interprets in a large measure the experimental results on scattering in regard to the state of polarisation, the intensity, and the spatial characteristics of the scattered beam, does not admit of any difference in the frequencies of the primary and the scattered radiation. A simple and quantitative explanation of this difference is obtained, however, if, as Compton and Debye have suggested, the act of scattering be regarded as a "collision" between a light quant and an electron. The X-ray quant of frequency ν has before the collision a linear momentum of $h\nu/c$. Part of this momentum is transferred to an electron with which it collides, and the light quant then rebounds with a smaller momentum, a smaller energy, and therefore a smaller frequency than before.

Of special significance is Compton's experimental proof that in the individual act of scattering of X-rays by an electron the direction of recoil of the electron is coupled with the direction of the scattered radiation in accordance with the ordinary mechanical principles of elastic collisions. This result appears to constitute a most direct and convincing proof of the light quant hypothesis.

Whilst the extreme light quant hypothesis has proved exceedingly useful in the interpretation of a great variety of phenomena which involve the transformation of radiant energy into other forms of energy, it has so far met with very little success in explaining the more purely optical characteristics of radiation such as its dispersion, interference, diffraction, and polarisation. These are just the characteristics, however, in the interpretation of which the continuous wave theory is found to be so eminently consistent and satisfactory. A beam of radiant energy, therefore, presents the anomaly that in the matter of its propagation it exhibits all the properties which we associate with a continuous wave train, yet in other respects it behaves as if the energy were localised only at certain selected points in the beam.

The reconciliation of these dualistic rôles of radiation has not yet been effected, although it appears possible that the clue to the solution of the problem may be found in the concepts underlying the new "quantum mechanics" of Heisenberg and Dirac or the "wave mechanics" of Schrödinger. We cannot, however, attempt any discussion of these most recent developments of the quantum theory which, demanding as they do a specialised mathematical equipment (and possibly involving a fresh philosophical outlook), would appear to lie outside the interest of the present-day chemist. It is improbable that the chemist will desire any other picture of sub-atomic phenomena than that supplied by the now classical Bohr theory, which, without inquiring too closely into the ultimate mechanism of the processes concerned, attempts to correlate all quantum phenomena in terms of one or two simple laws. True, the Bohr theory, by virtue of the formal character of the postulates which it involves, is necessarily limited in its scope, and even within its legitimate range is not always in accord with observation. In those particulars wherein the new theories are definitely more successful as regards result than the old, it will, however, be sufficient for our purpose to indicate the necessary modifications in formal treatment, without discussing their ultimate physical or philosophical import.

BOHR'S THEORY OF THE ORIGIN OF SPECTRAL LINES.

This may be regarded as a rational extension of Planck's results expressing the behaviour of the ideal linear oscillator in a radiation field to the problem of the interaction of radiation with the actual atomic and molecular models which we now believe to represent the ultimate units of matter. Starting from the fundamental conception of the electrical nature of matter, the conviction has gradually been established, through the correlation of a large variety of sub-atomic phenomena, that the neutral atom of any element consists of a minute core or nucleus of positive electricity surrounded by an atmosphere of electrons. The number of these electrons in the neutral atom is identical with the atomic number of the element; their total negative electrical charge exactly balances that of the positive nucleus. Although the bulk of the mass of the atom is associated with the nucleus, the physical dimensions of the latter are exceedingly small, and the "size" of the atom is determined not by the nucleus but by the spatial dimensions of the electron atmosphere about it. The simplest atom is that of hydrogen which consists of a nucleus and one electron only. These are held together by the Coulomb force of attraction, but considerations of mechanical stability require a compensation in some way of this force of attraction in the stable state of the system. Unless we make the arbitrary assumption of a hitherto unknown force of repulsion between unlike charges, operating only under sub-atomic conditions, we must regard the electrical force of attraction between the nucleus and the electron as being balanced by a centrifugal force due to rapid rotation of the electron in a circular or elliptic orbit around the massive nucleus. This is the dynamical model of the hydrogen atom originally proposed by Rutherford. An immediate difficulty, however, arises in that an infinite continuum of states of rotation of the electron about the nucleus is mechanically possible (depending upon the arbitrary initial conditions assumed), to each of which states there corresponds a definite planetary orbit of the electron and a definite energy content of the system. This is the first objection which can be urged against the Rutherford model—there is apparently no unique orbit of rotation of the electron which should be characteristic of the normal state of the atom. However, this is not the only objection to the model. It might be imagined that a definite state of rotation, once initiated, should continue indefinitely in the absence of external influences, and indeed this would be so were the attractions between the parts of the system other than electrical in nature. Classical electrodynamical theory demands, however, that by virtue of the acceleration to which the rotating electron is always subject, the system should be continuously emitting electromagnetic radiation. Such emission would, however, involve a gradual loss of energy by the system, and so the continued maintenance of a definite state of rotation by the isolated atom appears to be precluded. Rather, the electron should gradually lose its energy of rotation by emission of radiation, and since it must then simultaneously contract its orbit to satisfy the elementary requirements of mechanics, it should ultimately fall into the nucleus. The same is true for any more complex system of electrically charged particles moving relatively to one another. None of the mechanically conceivable motions of the constituent parts relative to one another can, according to classical views, correspond to a really stable configuration of the system.

Bohr's Stationary States.—We know from experience that no such catastrophic fate as the above does overtake the ordinary chemical atom, and we further know that at least one state—the normal state—exists in which the atom exhibits a complete and durable stability in the absence of external influences and does not emit radiant energy. If then we are to retain the useful features of the Rutherford dynamical model of the atom, we must obviously qualify in some way the criteria of stability which classical electrodynamics prescribes. The necessary modifications are formally expressed in the first postulate of Bohr's theory of atomic structure :—

Not all the kinematically conceivable states of motion of an isolated atom are physically possible. There is, however, a discrete series of states—the so-called quantum or stationary states—in which the atom can exist for a finite duration of time. In any of these states the atom possesses a peculiar, non-dynamical stability in the sense that any permanent change in its condition involves a complete transition from the stationary state in question into another stationary state.

It is implied in this postulate that the internal motion of the isolated atom in any stationary state is primarily governed by the laws of classical mechanics, with the sole exception that *the classical dissipation of energy by emission of radiation is forbidden.* The physically possible stationary states of the atom are a series selected out of all the dynamically possible modes of motion of the system, and are characterised by the fact that they conform to certain quantum conditions of restriction as well as to the usual kinematic laws of motion. Thus the possible quantum or stationary states of the simple harmonic Planck oscillator already dealt with are apparently given by the ordinary laws of mechanics taken in conjunction with the quantum restriction principle that the energy equals $nh\nu$, where n is any positive whole number. Other dynamically conceivable states of vibration of the oscillator are to be regarded as having no physical existence, or at most as transitory conditions of the system; and any permanent change which the oscillator undergoes is such as to leave it always in one or other of the quantised stationary states. For the circular vibration of an electron round a nuclear centre of attraction, the quantum equation of restriction suggested by Bohr takes the form

$$\text{angular momentum of rotation} = \frac{nh}{2\pi},$$

where n is again a $+^{\text{ve}}$ whole number, and h is the same Planck constant. For a hydrogen-like atom or ion, consisting of a single electron of mass m and charge $-e$ rotating about a massive nucleus of charge $+Ze$, this condition superimposed upon the ordinary equations of motion of the system then leads to a discrete series of physically possible states of rotation of the electron. These are such that the radii of successive orbits of the electron are as the squares of the natural numbers :—

$$r_n = \frac{n^2h^2}{4\pi^2Ze^2m} \quad . \quad . \quad . \quad . \quad (12)$$

$$(n = 1, 2, 3, 4 \ldots)$$

and the frequencies of rotation of the electron in the successive orbits are inversely as the cubes of the natural numbers :—

$$\nu_n = \frac{4\pi^2Z^2e^4m}{n^3h^3} \quad . \quad . \quad . \quad . \quad (13)$$

With widening orbit, the total energy content of the system progressively increases. There are two ways of representing the value of this energy, depending upon which state of the system is most conveniently taken as that of the zero level of energy. If energies be measured relative to that of the normal ($n = 1$) state of the system, then the energy in any state n is positive and is given by

$$E_n = AZ^2\left\{1 - \frac{1}{n^2}\right\} \quad . \quad . \quad . \quad . \quad (14)$$

where $A = 2\pi^2e^4m/h^2$. If, however, the zero level of energy be taken as that for which the charges $-e$ and $+Ze$ are completely separated and at rest relative to one another, then the energy content of the system in any quantised state n is negative and is given by

$$-W_n = -\frac{AZ^2}{n^2} \quad . \quad . \quad . \quad . \quad (15)$$

where W_n itself represents the work which would have to be performed on the system in the state n to separate the charges and bring them to rest at infinite distance apart. The two values for the energy E_n and $-W_n$ only differ, of course, by the constant quantity AZ^2 which represents the difference in the two zero levels.

Quantum Equations of Restriction.—Naturally, it is a matter of first importance in relation to the above principle of stationary states to find the general laws of quantum restriction to which any mechanical system will conform and which, for a given atomic model, will serve to select the physically possible modes of internal motion of the constituent particles. The concept of a special selection out of all the dynamically possible states of motion permitted by classical dynamics would be of little practical value if each freshly examined system required its own peculiar quantum equations of restriction. At first sight there does not appear to be any very obvious connection between the quantum equation of restriction successfully used by Planck for the linear vibration of the electron in the simple harmonic oscillator and that suggested by Bohr for the circular rotation of the electron in the hydrogen atom. Actually, however, these two are but special and artificial forms of a more general law of quantisation, applicable not only to these simple types of motion of one degree of freedom but also to the more complex motion of multiply periodic or conditionally periodic systems of any number of degrees of freedom. In order to appreciate the general statement, it will be necessary to indicate briefly how the configuration and motion of any mechanical system are defined in general dynamical theory.

A mechanical system of f degrees of freedom is one which has f distinct capacities for motion, and for which it is therefore necessary to specify f independent variables in order to define its position and configuration at any instant. The f variables chosen are termed the *generalised co-ordinates* or simply the co-ordinates of the system. A point particle free to move about in space has three degrees of freedom, and as its generalised co-ordinates we might choose either its Cartesian co-ordinates (x, y, z) or its polar co-ordinates (r, θ, ϕ). A rigid body has six degrees of freedom, three of translation and three of rotation, and its generalised co-ordinates might be chosen as the (x, y, z) of its centre of gravity, and three angle variables denoting its orientation in space. Corresponding to each co-ordinate we have a velocity component. If $q_1, q_2, \ldots q_f$ represent the generalised co-ordinates of any system, the *generalised velocity components* are given by $\dot{q}_1, \dot{q}_2, \ldots \dot{q}_f$, where $\dot{q}_i = \frac{dq_i}{dt}$. The kinetic energy T of the system is always capable of expression as a quadratic function of these $\dot{q}$'s by a relation of the form

$$2T = a_{11}\dot{q}_1^2 + a_{22}\dot{q}_2^2 \ldots + a_{ff}\dot{q}_f^2 + 2a_{12}\dot{q}_1\dot{q}_2 + 2a_{13}\dot{q}_1\dot{q}_3 + \ldots \quad . \quad (16)$$

wherein the coefficients a_{11}, a_{22}, a_{12}, etc. may be functions of the q's but not of the $\dot{q}$'s. For instance, for the point particle with three degrees of freedom

$$2T = m\dot{x}^2 + m\dot{y}^2 + m\dot{z}^2,$$

or

$$2T = m\dot{r}^2 + mr^2\dot{\theta}^2 + mr^2 . \sin^2\theta . \dot{\phi}^2,$$

depending upon whether the co-ordinates selected to represent the system are (x, y, z) or (r, θ, ϕ).

Again, corresponding to each generalised co-ordinate and velocity q_i and $\dot{q}_i$ we have a generalised component of momentum p_i defined by

$$p_i = \frac{\partial T}{\partial \dot{q}_i} \quad . \quad . \quad . \quad . \quad (17)$$

In the general case, each p is obviously a function of all the q's and $\dot{q}$'s and is linear with respect to the latter. From the above definitions it readily follows that when a generalised co-ordinate q_i is a linear co-ordinate, as for example an x, y, or z, the corresponding generalised momentum p_i is simply the component of linear momentum in the direction of the axis of that co-ordinate. When q_i is an angle variable, as θ above, then p_i becomes an angular momentum.

Now, if the motion of the system is periodic with respect to one of the co-ordinates, say q_1, then, so far as it depends upon this variable, the motion requires to be quantised, and only those dynamical conditions of the system are physically possible which conform to the quantum equation of restriction

$$\oint p_1 . dq_1 = n_1 h \quad . \quad . \quad . \quad . \quad (18)$$

where n_1 is any positive integer. The symbol $\oint$ denotes that the integration is to be effected over a complete period or libration of the q_1 co-ordinate. It may be shown that this single relation embodies the two previously mentioned and apparently dissimilar rules of quantisation used by Planck and Bohr respectively. Again, if the dynamical system is multiply periodic in character, so that a number of the co-ordinates q_1, q_2, q_3 . . . repeat themselves in value after definite periods, the only possible modes of motion of the system are those for which the following conditions are simultaneously valid :—

$$\left.\begin{aligned} \oint p_1 dq_1 &= n_1 h, \\ \oint p_2 dq_2 &= n_2 h, \\ \oint p_3 dq_3 &= n_3 h, \text{ etc.} \end{aligned}\right\} \quad . \quad . \quad . \quad (19)$$

The quantum numbers n_1, n_2, n_3 . . . are independent positive integers. It should be emphasised that these quantum conditions of restriction apply to periodic types of motion only. For non-periodic types of motion there are apparently no corresponding equations of restriction, and any of the infinite continuum of dynamically possible states are also physically possible states.

Sommerfeld's Modification of the Bohr Atom Model.—The general quantum equations of restriction for periodic systems in the above form were first enunciated by Wilson and by Sommerfeld, and applied by the latter to the Rutherford model of the hydrogen atom with *elliptical* rotation of the electron round the nucleus. When Bohr's simplifying assumption of circular rotation is dropped, the motion of the electron in the H atom involves two degrees of freedom and two co-ordinate variables, which may conveniently be chosen as the polar co-ordinates (r, θ) of the electron with respect to the nucleus as origin. Two quantum equations of restriction are then demanded, and the possible stationary states of rotation of the electron work out as ellipses or circles whose parameters are determined by two quantum numbers, n_a and n_r. These partial quantum numbers are termed the *azimuthal* and *radial* quantum numbers respectively. The energy of the system is determined by the value of the *total* or *principal* quantum number $n = (n_a + n_r)$; the type of the electron's orbit by the separate values of n_a and n_r. The orbit (n_a, n_r) is an ellipse with semi-major and semi-minor axes a and b which are given by

$$\left.\begin{aligned} a &= \frac{h^2}{4\pi^2 e^2 m}(n_a + n_r)^2 \\ b &= \frac{h^2}{4\pi^2 e^2 m} n_a(n_a + n_r) \end{aligned}\right\} \quad . \quad . \quad . \quad (20)$$

e and m being the charge and mass of the electron and h the Planck constant. From these expressions for a and b it is clear that the electron's orbit becomes circular ($a = b$) for $n_r = 0$, and that the eccentricity of the orbit is the greater the greater n_r is. Also, any orbit for which n_a is zero is obviously forbidden since it would represent a linear vibration of the electron through the nucleus. The energy content of the atom in the stationary state (n_a, n_r) is given by

$$E_{n_a, n_r} = A\left\{1 - \frac{1}{(n_a + n_r)^2}\right\} \quad . \quad . \quad . \quad (21)$$

where $A = \frac{2\pi^2 e^4 m}{h^2}$. Here the state for which $n = (n_a + n_r) = 1$ represents the state of least energy content, that is, the normal state of the atom, and this is taken as the zero level of energy in computing the energy of the atom in any other state. Alternatively the energy of the system is represented by

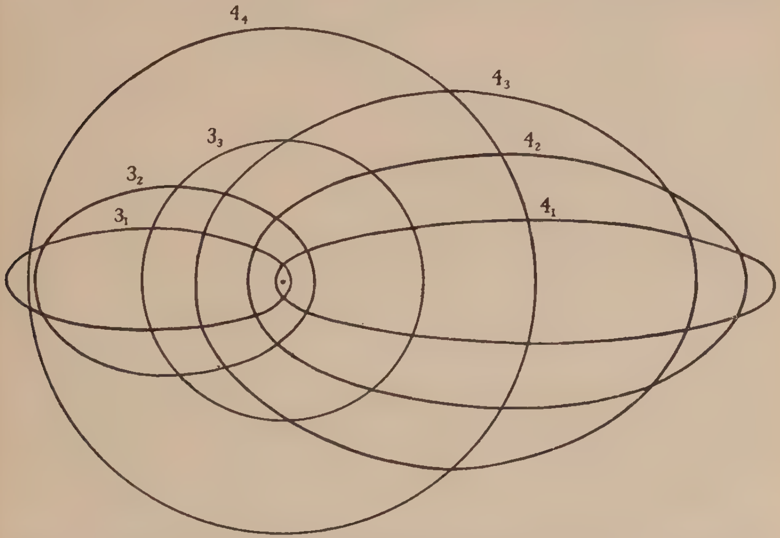

FIG. 11.—Possible orbits of the electron in the hydrogen atom corresponding to $n = 3$ and $n = 4$ (n_k designation).

$$-W_{n_a, n_r} = -\frac{A}{(n_a + n_r)^2} \quad . \quad . \quad . \quad (22)$$

where the zero level of energy content is that of the state wherein the charges are completely separated and at rest. Since the value of E_{n_a, n_r} is determined by the sum $(n_a + n_r)$ but not by the separate values of n_a and n_r, it follows that all orbits, whether circular or elliptic, for which the *total* quantum number $(n_a + n_r)$ is the same, represent identical energy levels of the atom. There is but one orbit—a circle—for which $n_a + n_r = 1$, two orbits—a circle and an ellipse—for which $n_a + n_r = 2$, three orbits—a circle and two ellipses—for which $n_a + n_r = 3$, etc. (cf. Fig. 11). However, the shapes of the orbits, as distinct from the possible energy levels of the atom which they characterise, depend upon the separate values of n_a and n_r; otherwise expressed, upon the value of the total quantum number $n = n_a + n_r$ and also upon that of the azimuthal quantum number n_a. This latter quantum number is more usually written as k, and the orbit n_k is that for which the total quantum number is n and the azimuthal quantum number is k. This orbit is from equations (20) an ellipse with major and minor axes in the ratio n/k. Obviously the orbits for which $k = n$ are circles, and the eccentricity of any orbit increases as k diminishes relatively to n. Finally, it is important to note that the angular momentum of the electron in any n_k orbit is now given, not by $nh/2\pi$ as in the original quantum equation of restriction of Bohr, but by $kh/2\pi$. The net result can be expressed by saying that the energy of the electron is quantised by the total quantum number n, and its angular momentum is also quantised by the azimuthal quantum number k.

Bohr's Frequency Condition.—Having indicated the nature of the quantum laws which determine the various stationary states of the simplest atom model, we must now proceed to adduce some evidence of the physical reality of these states. At least one stable or stationary state of any atom—its normal state—is required by the invariance of its physical and chemical properties. The existence of a further series of stationary states in which the atom possesses energy in excess of its normal amount appears to be demanded by certain of its physical reactions, in especial, by the relations governing the exchange of energy between the atom and a field of electromagnetic radiation. It is not sufficient to accept only the one stationary state of the atom, representing a minimum energy content and a physically inexplicable stability of the electrical system. Classical electrodynamics would then require that such an atom should absorb from a field of radiation that frequency which is identical with the frequency of rotation of the electron, and since this latter frequency ought to decrease continuously as the radius of the orbit increases with continued absorption of energy, the atom should exhibit a continuous absorption spectrum sharply limited only on the high frequency side. The emission spectrum of the atom should be of an exactly similar nature. In disagreement with this, however, the atom is found to give *line* absorption and *line* emission spectra ; it interacts only with a discrete series of monochromatic radiations.

The stationary states of Bohr's first postulate are states of definite energy content, so that the atom when in any given stationary state cannot absorb or emit radiant energy and remain therein. Rather, any permanent change in the condition (energy content) of the atom must involve a complete transition from one stationary state to another. In particular, then, the absorption or emission of radiant energy must be accompanied by such a transition, and this for the isolated atom implies the appearance or disappearance of a finite amount of radiant energy equal to the difference in the energy contents of the atom in the two states.

Bohr's second postulate now relates this energy loss or gain on the part of the atomic system more particularly to the *quality* of the radiation involved :—

When a transition between two stationary states is accompanied by the emission or absorption of radiant energy, the radiation is monochromatic in character and of a frequency ν *given by*

$$h\nu = E'' - E' \quad . \quad . \quad . \quad . \quad (23)$$

where E' *and* E'' *are the total energy contents of the atom in the initial and final states.* Otherwise expressed, the change in the energy content of the atom is accompanied by the destruction or appearance of one quantum of monochromatic radiation.

Without considering as yet the implications of this second postulate in relation to classical theory, we may examine with its aid some of the experimental evidence for the existence of discrete stationary states of the atom. One of the most important pieces of evidence in this connection is contained in the *Ritz Principle of Combination*—a law common to all line series spectra and formulated by Ritz some years before the development of modern quantum theory. The Principle states that the frequency of every line of a series spectrum can be expressed as the difference between two terms ; and, with certain exceptions, each difference between any pair of such terms is the frequency of an observed line. This composite structure of a spectral line, whilst entirely foreign to the requirements of classical theory, receives a ready interpretation if the production of the line is regarded as accompanying a transition of the radiating mechanism from one discrete stationary state to another. In this case, the two independent terms of each spectral line must obviously be related to the two values of some property of the system in its initial and final states, and, from the nature of the Bohr frequency relation, the property in question is undoubtedly the energy level of the system. Which of the two combining terms in any spectral line corresponds to which of the two combining energy levels is a question which will be decided presently.

The Series Spectrum of Hydrogen.—Considering now the hydrogen atom, its various stationary energy levels are given by

$$E_n = \frac{2\pi^2 e^4 m}{h^2}\left\{1 - \frac{1}{n^2}\right\} \quad . \quad . \quad . \quad (24)$$

where n—the total quantum number—may be any positive whole number including unity. Combining this expression for E_n with the Bohr frequency condition, it is seen that the frequencies of all the lines in the emission spectrum of the hydrogen atom should be represented by the formula

$$\nu = \frac{2\pi^2 e^4 m}{h^3}\left(\frac{1}{n'^2} - \frac{1}{n''^2}\right) \quad . \quad . \quad . \quad (25)$$

with $n'' > n'$.

Taking successively the various possible transitions of the excited hydrogen atom from orbits of higher quantum number to the 1st, 2nd, 3rd . . . orbits respectively, we then obtain the predicted spectral series :—

$$\nu = \frac{2\pi^2 e^4 m}{h^3}\left\{\frac{1}{1^2} - \frac{1}{n''^2}\right\}; \quad n'' = 2, 3, 4, 5 \ldots$$

$$\nu = \frac{2\pi^2 e^4 m}{h^3}\left\{\frac{1}{2^2} - \frac{1}{n''^2}\right\}; \quad n'' = 3, 4, 5, 6 \ldots$$

$$\nu = \frac{2\pi^2 e^4 m}{h^3}\left\{\frac{1}{3^2} - \frac{1}{n''^2}\right\}; \quad n'' = 4, 5, 6, 7 \ldots$$

Comparing these predicted series of lines with the Lyman, Balmer, and Paschen series (cf. p. 18), it is seen that the agreement between theory and observation is complete, provided only that the Rydberg constant R, which is the constant numerical factor of all three series, is equal to the factor $\frac{2\pi^2 e^4 m}{h^3}$. The Rydberg constant R, in frequency units, is experimentally observed to be $3{\cdot}29 \times 10^{15}$ sec.$^{-1}$. The value of $\frac{2\pi^2 e^4 m}{h^3}$ with e, m, and h derived from data which are quite independent of optical measurements is $3{\cdot}28 \times 10^{15}$ sec.$^{-1}$. The very slight difference in these two numerical values lies well within the limits of error of measurement of e, m, and h. Besides the above-mentioned series of hydrogen lines, a few lines belonging to the series $\nu = R\left(\frac{1}{4^2} - \frac{1}{n''^2}\right)$ have been observed by Brackett in the infra-red emission spectrum of hydrogen. In terms of our theory, these lines derive from transitions of the electron in the hydrogen atom from upper orbits to the $n' = 4$ orbit.

All the lines in the series spectrum of hydrogen are obtained from the various possible combinations in pairs of the terms

$$\frac{R}{1^2}, \frac{R}{2^2}, \frac{R}{3^2}, \frac{R}{4^2} \ldots$$

The theoretical significance of these spectral terms now follows. The term R/n^2 corresponds to the energy level of the atom for which the total quantum number of the rotating electron is n, and this term, when multiplied by the constant h, is numerically equal to W_n, the *negative* value of the energy of the atom in this state. It is important to note that the spectral term does not correspond to the energy of the state to which it refers but to the negative value of this energy. For this reason the larger of two combining spectral terms corresponds not to the upper but to the lower of the two combining energy levels of the atom. The spectral term is, in fact, a measure of the work required to effect the ionisation of the atom in the state to which it refers.

In the above we have made no distinction, so far as the spectral line is concerned, between states of excitation of the hydrogen atom of the same principal quantum number n but different azimuthal quantum numbers k, that is, between circular and elliptic orbits of the electron, since from equation (21) the energy E_{n_a, n_r} or $E_{n, k}$ of the atom depends only upon n and not upon k. Actually, however, this expression for $E_{n, k}$ is not quite exact, because in its deduction the "relativity" effect of the velocity of the electron upon its mass is left out of account. When allowance is made for this effect, the resulting value of $E_{n, k}$ is found to differ from that which we have used by additional terms of very small magnitude which involve not only n but also k. It follows that the frequency emitted by the hydrogen atom in changing from the state $n''_{k''}$ to the state $n'_{k'}$ should depend not only upon the values of n'' and n' but also to a small extent upon those of k'' and k'. Although the smallness of the expected effect makes a complete test of this conclusion difficult, it is nevertheless found that under very powerful dispersion the lines of the Balmer series are not single lines but are composite in character. Each line appears as a very narrow doublet, the separation of the two components being the same for all lines of the series and equal to 0·36 cm.$^{-1}$. This doublet structure of the Balmer lines is interpreted to correspond to the two possible end states of the atom, viz. $n' = 2$, $k' = 2$ (circular orbit) and $n' = 2$, $k' = 1$ (elliptic orbit), which can be involved in the emission of each line of the series. The observed doublet separation is in quantitative agreement wlth the value calculated on this basis. The further fine structure of each line which should result from the different possible values of k'' for each value of n'' is on too small a scale to be observed.

The lines of the Lyman series, unlike those of the Balmer series, exhibit no fine structure under the highest dispersion. Specially significant is the lack of fine structure in the first line of this series which derives from the transition $n'' = 2 \rightarrow n' = 1$ and which, corresponding to the two possible values of k'' of 2 and 1, should be a doublet with the same separation of the components as the doublets of the Balmer series, viz. 0·36 cm.$^{-1}$. The absence of fine structure in the Lyman lines provides one illustration of a restriction upon the possibilities of combination of spectral terms in emission which is of general applicability. Only those terms combine to give spectral lines which involve a change in the azimuthal quantum number k of one unit: $\Delta k = \pm 1$. In the case of the Lyman lines $k' = 1$, and for each value of n'' there is only one possible value of k'', viz. $k'' = 2$, which satisfies this condition. This restriction rule is considered in more detail later in relation to optical series spectra in general.

The fine structure of the hydrogen lines, though practically insignificant, is naturally of considerable theoretical importance, inasmuch as it requires for its explanation the actual existence of elliptic as well as circular orbits of the electron in the atom. The explanation of the Stark and Zeeman resolutions of the hydrogen lines under the action of electric and magnetic fields respectively also requires the two types of electronic orbits. An adequate discussion of these effects cannot however be given here; for details the reader must be referred to any of the works mentioned at the end of the Chapter.

We may now restate in general terms the quantum interpretation of the origin of the series spectrum of hydrogen. The emitting unit is the neutral hydrogen atom, the normal state of which corresponds to an electron orbit for which $n = 1$. This represents the lowest energy level of the atom, and its actual occurrence is evidenced by the constant spectral term $R/1^2$ in the Lyman series. Excitation of the atom as a preliminary to emission involves transfer of the electron from this normal to an outer orbit—in the limit, to complete separation of the unlike charges. Reversion in a single stage of the electron from an outer to an inner orbit is accompanied by emission of a single spectral line. Alternatively, however, the transition between two orbits may take place in steps, involving the consecutive emission of two or more lines by the same primarily excited atom; for example, the electron might first revert to the third, thence to the second, and finally to the normal orbit with consecutive emissions, first of some line of the Paschen series, then of the first lines of the Balmer and Lyman series in order.

The convergence frequency of the Lyman series is the spectral term $R/1^2$ itself, and this, when multiplied by h, represents the energy necessary to ionise the normal hydrogen atom and leave the separated charges at rest with respect to one another. The single act of reversion of this system to re-form the normal atom should be accompanied by emission of a frequency equal to the convergence limit itself. Similarly, the recombination of the stationary separated charges to leave the re-formed atom with the electron in the second orbit should involve the emission of the convergence frequency of the Balmer series. Under the usual conditions of ionisation, however, the free electron which is finally to unite with the hydrogen nucleus may have any velocity and therefore any kinetic energy (E_t) with respect to the latter. The energy which it gives up as radiation in passing from the free state into a definite quantum orbit around the nucleus may, therefore, have any value *above* that which corresponds to the same binding of an electron starting from rest. If the Bohr frequency relation is to be preserved under these conditions, the continuous manifold of original states of energy content of the system, combined with the definite quantised end state, must involve the possibility of a *continuous* region of emission, described mathematically by the expression

$$\nu = \nu_c + \frac{E_t}{h} \quad . \quad . \quad . \quad . \quad (26)$$

lying above the convergence frequency ν_c corresponding to that end state. Such a continuous range of emission is indeed observed in certain stellar spectra, beginning at the convergence limit of the Balmer series (360 $\mu\mu$) and stretching far into the ultra-violet; the same has also been obtained by Stark by excitation of hydrogen to emission by bombardment with canal-rays. In both cases the conditions are such that not only dissociation of the hydrogen molecule into atoms, but also complete ionisation of the atoms, is easily possible.

Absorption by Hydrogen Atoms.—Granted that a certain discrete series of stationary states of the atom are alone physically possible and that the emission of radiation conforms to the Bohr frequency relation, the reciprocal nature of emission and absorption requires that the latter process should also be governed by quantum laws. By absorption of radiation the atom must pass from a lower quantised to a higher quantised energy level, absorbing as it does so only radiation of the same frequency as would be emitted in the reverse change; from Bohr's second postulate this frequency is given as the difference in the energy contents of the absorbing system in its initial and final states, divided by h.

The absorption spectra of most substances in the atomic state are much less complex in form than their emission spectra. Whereas the totality of emission lines observed under given conditions of excitation may belong to several different line series, all the lines in the absorption spectrum of an atom normally belong to one series only. Under such conditions of emission as are provided by excitation with the electrical discharge, various states of excitation of the atom are usually possible, and therefore emission lines may appear corresponding to all the possible transitions between the highest state attained by the atom, intermediate states, and the normal state. In absorption measurements at ordinary or even moderately high temperatures, however, practically all absorbing atoms start from the same initial state—the normal state. All the absorption lines should, therefore, have a common term, that is, they should belong to the same optical series.

The absorption spectrum of unexcited hydrogen atoms should, therefore, consist of a series of lines lying in the ultra-violet and corresponding exactly in wave-length with the lines $\nu = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$ of the Lyman emission series of hydrogen, indicating transitions by absorption of the electron from its normal ($n = 1$) orbit to orbits of higher quantum number. Unfortunately the extreme conditions required, whether by high temperature or by electronic bombardment of hydrogen molecules in a discharge tube, for the maintenance of any appreciable concentration of atomic hydrogen preclude the experimental verification of this predicted reversal of the Lyman series in absorption. It is, however, possible to obtain with hydrogen absorption lines which are the reversals of certain lines in the Balmer emission series. Such absorption lines—characteristic of the already excited atom as the absorbing unit—are actually observed as the Fraunhofer C, F, and H lines in the sun's spectrum and also in the spectra of certain stars. The C, F, and H Fraunhofer lines represent the reversals of the first three lines H_α, H_β, and H_γ of the Balmer emission series of hydrogen. Here what is obviously happening is that from the continuous emission spectrum coming from the interior of the star, an external atmosphere of hydrogen atoms, already thermally excited to the $n = 2$ quantum level, absorbs the monochromatic frequencies $\nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$. A similar reversal of the first members of the Balmer series may be obtained by various devices in the laboratory, for example, by using a long discharge tube containing hydrogen and fairly strong electrical excitation. For end-on observation of the tube, the discharge is then bluish-white in colour, although the normal colour of the hydrogen Geissler tube discharge, when viewed transversely, is a rose-red. What happens in the first case is that the red (H_α) line which is predominant in the emission is reabsorbed by the long column of excited hydrogen atoms in the tube. We shall later have occasion to mention other examples of absorption of radiation on the part of already excited atoms.

By the act of absorption of radiation, the atom is not restricted solely to transitions of the electron from its initial orbit to any of the virtual outer quantum orbits. Complete ionisation by absorption is also possible ; this is the case when the normal hydrogen atom absorbs the convergence frequency of the Lyman series. However, the condition of complete ionisation corresponds not to one but to an infinite continuum of possible end states, since the energy of translatory motion of the electron when freed from the atom residue is not restricted by quantum conditions. Accordingly, if the atomic system can pass in a single act of absorption from an initial quantised state to a state representing complete ionisation and any relative motion of the separated charges, the line absorption spectrum should continue as a region of continuous absorption beyond the convergence limit of the series of absorption lines. Any frequency absorbed in this continous region is represented mathematically by

$$\nu = \nu_c + x \quad . \quad . \quad . \quad . \quad (27)$$

with x continuously variable.

So far as hydrogen is concerned the demands of theory in this respect are satisfied in certain reversed star spectra. Here a reversal of the lines of the Balmer series is obtained (cf. above) and, starting from the convergence limit of the Balmer series of reversed lines, there is also observed a broad region of continuous absorption corresponding to the complete ionisation of the absorbing atoms. The same type of phenomenon is more readily examined with the vapours of the alkali metals where it is easily possible to obtain the free atoms under conditions suitable for the observation of their absorption spectra. With sodium vapour, for example, the absorption spectrum consists of a line series—the reversal of the Principal emission series of sodium—to the convergence limit of which is appended a region of continuous absorption which stretches well into the ultra-violet (cf. Chapter III.).

OPTICAL SERIES SPECTRA OF THE ELEMENTS.

So far we have restricted ourselves to discuss the hydrogen atom and its series spectrum from the standpoint of Bohr's theory. The only other optical line series spectrum which is structurally as simple as that of hydrogen is the spark spectrum of helium, the various lines of which are accurately described by the relation

$$\nu = 4R\left(\frac{1}{n'^2} - \frac{1}{n''^2}\right) \quad . \quad . \quad . \quad . \quad (28)$$

where R is again the Rydberg constant and n' and n'' are positive whole numbers. In terms of the foregoing principles, the mechanism operating in the production of this spectrum should consist of an electron capable of rotating in various stationary orbits about a central charge of *two* positive units ($Z = 2$). This system represents the singly ionised helium atom, and the spectroscopic evidence thus suggests that the configuration of the He^+ ion is essentially the same as that of the neutral H atom. The two systems differ only in dimensions, the possible orbits of the electron in He^+ being much closer to the nucleus because of the intrinsically greater force of attraction upon it. We have seen from the term structure of the Lyman series of hydrogen that the normal state of the H atom corresponds to that stationary orbit of the electron for which $n = 1$. No corresponding spectroscopic evidence regarding the normal state of ionised helium is available, since the helium spark series

$$\nu = 4R\left(\frac{1}{1^2} - \frac{1}{n''^2}\right)$$

has not yet been observed—this series would lie in the spectral region $31 - 23\ \mu\mu$ which has hitherto evaded examination. There is indirect evidence, however, from the ionisation potentials of helium, that the normal orbit of the electron in the ionised atom is here also that orbit for which $n = 1$.

The structures of neutral helium and of all the other chemical atoms which contain an outer atmosphere of more than one electron do not admit of the same precise treatment as do hydrogen and ionised helium. This is not due to the increasing complexity of the nucleus as the atomic number of the element increases. The nucleus, however complex in itself, can probably always be regarded, from the point of view of the field it presents to the surrounding atmosphere of electrons, as a very localised charge of positive electricity acting upon all electrons outside itself with the Coulomb force of attraction; but when there is more than one electron in the atom's atmosphere, their mutual actions must also be taken into account, and under these circumstances the dynamical analysis of the possible modes of motion of even the simplest system becomes extremely involved. With certain premises, indeed, a number of special solutions of the "many-body problem" can be obtained corresponding, for example, to a disposition of the electrons in one or more circular rings about the nucleus, or in independent but polyhedrally symmetrical orbits. Such solutions, however, do not conform to the criteria of mechanical stability, nor does it appear that the ordinary laws of mechanics and electrostatics can lead to any solution of the disposition, whether static or dynamic, of a number of electrons about a positive nucleus, which will be stable in the mechanical sense—this, be it noted, quite apart from the inherent instability which classical electrodynamics prescribes for any system of electrically charged particles of this nature moving relative to one another. Bohr's first postulate begins indeed by denying the applicability of classical electrodynamics to atomic phenomena, so that the criteria of stability demanded by classical electrodynamics no longer enter into the problem. The postulate then proceeds to establish a quantum principle of restriction to which all multiply periodic systems should conform, and which enables us to select, from all the mechanically possible and stable states of a system, those states which can be physically realised. For anything beyond the two-body problem, however, the older mechanics and electrostatics do not afford *any* possible stable states of the system from which such a selection can be made, and it therefore becomes necessary to modify the basic mechanical principles or the electrostatic laws of attraction and repulsion between like and unlike charges before quantum equations of restriction can be applied quantitatively to the solution of the problem under consideration.

Our present admittedly qualitative ideas regarding the structures of the atoms are based partly upon an application of Bohr's two postulates to the details of their optical series spectra, partly upon legitimate inferences which can be drawn from their known physical and chemical properties. The hydrogen spectrum and the ionised helium spectrum receive quantitative interpretation in terms of a number of discrete stationary states of the atom, each of definite energy content and each involving a different orbit of the single electron round the nucleus, and the terms in the spectral series are found to be simply related to these different energy levels of the atom. The largest term in the spectrum is that which corresponds to the lowest energy level, and quantitatively the negative value of each term gives a measure of the energy of the system in the corresponding stationary state, the zero of energy being taken as that of the system for infinite separation of the charges at rest relative to one another. The general applicability of the Ritz Principle of Combination to the series spectra of the other elements, which Principle must imply that some fundamental significance attaches to the spectral terms, now suggests that these spectra also owe this characteristic term structure to the existence of a series of definite energy levels of the atom, given quantitatively by the negative values of the terms in the spectrum. The general similarity in form of the spectral terms to those of the hydrogen and ionised helium spectra further suggests that the essential feature of each stationary state of any atom is the orbit of one single electron relative to the rest of the atom. The transitions of this—the optical or radiating electron—from one quantised orbit to another would then be the source of the spectral lines of the element considered. Finally, the fact that the numerator of each term in the arc spectrum of any element is the same in value as the Rydberg constant for hydrogen, while the numerator of each term in the spark spectrum of the same element is equal to that in the spectrum of singly ionised helium, points to the radiating electron in optical spectra being always one of the outer electrons in the electron atmosphere of the atom.

The Azimuthal Quantum Numbers of Spectral Terms.—With these premises, we may now examine the various terms of a spectral series in respect of the different types of electron orbit to which they are likely to correspond. The action of the atom residue upon the radiating electron can to a first approximation be regarded as that of a central, spherically symmetrical field of force in which the electron moves. The general solution of the possible *periodic* motions of such a system corresponds to a series of non-reëntrant rosette paths of the electron round the centre of force. Roughly, each orbit may be described as an ellipse the perihelion of which undergoes a uniform rotation round the centre of force in the same plane as the orbit. The closed elliptical orbits of the electron in the hydrogen atom are a special case of this motion for a strictly Coulomb field of force. When the motion of the electron is quantised, the size and shape of the orbits are again fixed by two quantum numbers n and k. To a first approximation the first of these—the total or principal quantum number—determines the major parameter of the orbit and the energy content of the system. The second—the azimuthal quantum number—again determines the angular momentum of the electron in its orbit by virtue of the relation

$$\text{angular momentum} = \frac{kh}{2\pi},$$

and the ratio n/k again decides the shape of the orbit, i.e. its eccentricity. If now the energy of the system, comprising an electron and an atom residue of net charge equal to Z positive units, is written in a form analogous to equation (15), viz.

$$-W_n = -\frac{AZ^2}{n^{*2}} = -\frac{RhZ^2}{n^{*2}} \quad . \quad . \quad . \quad (29)$$

then the "effective" total quantum number n^* of the state is no longer equal to the true total quantum number n, as in the case of hydrogen, but differs from n by a non-integral correction term δ. Provided the deviation of the central field from the Coulomb law of attraction is not large, this correction term is small, and its value depends only upon the azimuthal quantum number k of the orbit and not upon n. Further, δ is the smaller the larger the value of k. The spectral term $\frac{RZ^2}{n^{*2}}\left(=\frac{W_n}{h}\right)$, which according to the Bohr frequency relation characterises the orbit, should therefore be the more hydrogen-like, i.e. the more nearly equal to RZ^2/n^2, the larger the value of the azimuthal quantum number k.

This same result can be expressed in more qualitative fashion as follows. The force exerted by the atom residue upon the radiating electron will, for sufficiently great separation of residue and electron, be practically a Coulomb force, but will deviate from this the more the closer the electron approaches to or actually penetrates into the atom residue in any part of its orbit. From Fig. 11 we see, however, that for the different hydrogen orbits of the same total quantum number n, the electron approaches the nucleus closest in the orbit of greatest eccentricity, i.e. of smallest azimuthal quantum number k. For any atom, therefore, the larger the value of k, the more of the electron's orbit is likely to be situated in the outer Coulomb part of the field, and the more will the spectral terms corresponding to such orbits resemble those of hydrogen.

It has already been noted in Chapter I. that the terms of any series spectrum arrange themselves empirically into S, P, D, and F sequences, the members of which are to a first approximation capable of expression in the form

$$\frac{RZ^2}{(\mathrm{n}+S)^2},\ \frac{RZ^2}{(\mathrm{n}+P)^2},\ \text{etc. } (Z=1 \text{ for arc, } Z=2 \text{ for spark, etc.}),$$

where n is a variable positive whole number for each sequence, and S, P, D, and F are sequence constants. If we compare this form of expression of a spectral term with the theoretical $\frac{RZ^2}{(n+\delta)^2}$ or $\frac{RZ^2}{n^{*2}}$, we can now draw certain conclusions regarding the nature of the electron orbits to which the S, P, D, and F terms correspond. In the first place, the fact that δ depends to a first approximation upon k only, suggests that the sequence constants S, P, D, and F are also functions of k only, and that the S, P, D, and F terms differ essentially in that they characterise electronic orbits with different values of the azimuthal quantum number. Accordingly, the sequence of S terms corresponds to a series of orbits of the radiating electron for which the total quantum number n progressively increases, but the azimuthal quantum number k remains constant. The sequence of P terms will refer to another such series of orbits characterised by a different constant azimuthal quantum number, and so on. The actual value of k for all the orbits of any particular sequence follows from a closer examination of the characteristics of the S, P, D, and F terms. Writing these for any element in the form RZ^2/n^{*2}, it is found that for most series spectra the effective quantum number n^* becomes the more nearly integral, i.e. the term itself becomes the more hydrogen-like, the further we proceed in the order S, P, D, F . . . This is illustrated by the data in Table I., which gives the effective quantum numbers n^* of the first S, P, D, and F terms in the arc spectrum of each of the alkali metals. The F

orbits are clearly the most hydrogen-like, the *D* orbits next in order, while the *P* and *S* orbits must approach close to the atom residue or even penetrate it. It follows that the azimuthal quantum number k increases progressively from *S* terms to *F* terms, and we are therefore justified in presuming that for *S* terms $k = 1$, for *P* terms $k = 2$, for *D* terms $k = 3$, and for *F* terms $k = 4$.

TABLE I.

	Value of n^* of the first (largest) term.			
	S.	*P.*	*D.*	*F.*
Li . . .	1·59	1·96	3·00	4·00
Na . . .	1·63	2·12	2·99	4·00
K . . .	1·77	2·23	2·85	3·99
Rb . . .	1·80	2·27	2·77	3·99
Cs . . .	1·87	2·35	2·55	3·98

With this allocation of azimuthal quantum numbers, we are in a position to restate an important principle which has been found empirically to govern the possibilities of combination of spectral terms to give emission lines. It has already been noted in Chapter I. that when the terms of series spectra are arranged in *S*, *P*, *D*, and *F* sequences, the only combinations which are normally observed in emission are those of *S* with *P*, *P* with *D*, and *D* with *F* terms. With the above interpretation of the nature of different terms, this restriction upon the Ritz Principle of Combination now admits of the alternative statement :—

Only those terms normally combine with one another to give a spectral line for which the values of k differ by unity, viz.

$$\Delta k = \pm 1.$$

We have reached this result by interpretation of the empirical facts of series spectra in terms of an admittedly crude conception of the radiating system responsible therefor. The same result is independently obtained, however, by application of Bohr's Principle of Correspondence to the same type of electronic motion as considered above. To give a detailed discussion of this Principle lies outside the scope of this work. Its substance and application to the present problem, may, however, be stated briefly.

The Principle of Correspondence.—The emission of radiant energy by a material oscillator is treated in classical electrodynamics as an essentially causal process. Not only the frequency of the emitted radiation, but also its intensity and its state of polarisation, are determined unambiguously by the instantaneous electrodynamical condition of the oscillator itself, and the emission of a definite quantity of radiant energy requires a definite time interval for its occurrence. In the quantum theory, however, the elementary process of emission is conceived of as a catastrophic and apparently non-causal event. The frequency of the radiation emitted by the oscillator in the transition between two discrete energy levels is indeed given by the Bohr frequency condition, but nothing is known regarding the details of the history of the oscillator during the transition, and not even a time interval can be ascribed to the catastrophic event. We cannot, therefore, speak of the intensity of emission of the oscillator at any instant. The oscillator apparently exists quiescent for some time in the upper quantum state, then it " decides " to emit, and, when it does so, it emits the whole quantum $h\nu$ in one event and is once more quiescent. To cloak our ignorance of the factors which determine whether or not the quantum transition will actually occur and if so how frequently, we speak of the " probability " of its occurrences in the same way as we speak of the probability of occurrence of a radioactive change, about which we know just as little. The probability of occurrence of the individual event then determines the gross intensity of emission of a system comprising a large number of similar oscillators each of which emits at some time or other a quantum $h\nu$ of radiation.

In spite of the radical dissimilarity of the two conceptions of the elementary processes of emission (and likewise of absorption) and the incompleteness of the quantum picture, the averaged results of quantum processes nevertheless degenerate to those of classical processes in the limit where the discontinuities inherent in the former become very fine-grained, that is, where the successive discrete energy levels of the material system differ very little from one another. An example of this has already been encountered in the applicability of the Rayleigh-Jeans law of black body radiation in the limit of small frequencies and high temperatures. Under these conditions the unit $h\nu$ by which the material oscillator can change its energy content is very small compared with the averge energy content itself of the oscillator, and therefore the interchange of energy between the oscillator and the radiation field assumes a practically continuous aspect. The " average " intensity of emission (or of absorption) of the quantum oscillator under these conditions becomes equal to the intensity of emission (or of absorption) of the corresponding classical oscillator. Another example of such degeneration is provided by the behaviour of the Bohr hydrogen atom for electronic orbits far removed from the nucleus. The frequency of the radiation emitted or absorbed in a transition of the electron between consecutive circular orbits is given by

$$\nu = \frac{2\pi^2 e^4 m}{h^3}\left\{\frac{1}{n^2} - \frac{1}{(n+1)^2}\right\} = \frac{2\pi^2 e^4 m}{h^3}\left\{\frac{2n+1}{n^2(n+1)^2}\right\}.$$

For very large values of n this becomes $\nu = \dfrac{4\pi^2 e^4 m}{n^3 h^3}$, which is numerically equal to the frequency of rotation of the electron in either orbit. According to classical theory, however, this is just the frequency of the radiation which would be emitted or absorbed by the system in either of these quantum states.

It follows from such examples as these that, in the limit of infinitely slow vibrations or rotations of any material model, both the frequency and the intensity of the radiation emitted in an essentially quantum transition are given by the corresponding classical quantities derived from the same model. This quantitative agreement in respect of the frequency emitted only holds, of course, when the combining energy levels are close together, that is, when the quantum numbers concerned are large. In general, the actual frequency emitted in a quantum transition between states characterised by small quantum numbers bears no simple relation to the natural frequency or frequencies of the system either in its initial or in its final state. Nevertheless, Bohr suggests that a correspondence, at least qualitative, should still exist between the intensity of the emission accompanying a given quantum transition between two stationary states and the intensities of certain correlated emission processes which classical theory would prescribe for the system in these same states.

In order to illustrate the nature of this correspondence, we may consider the case of a polar vibrator of one degree of freedom, similar to the Planck oscillator, but of anharmonic character. This implies that the electric moment **P** of the oscillator is not a simple harmonic function of the time, but it may be expressed analytically as a function of the time t in the form of a Fourier series :—

$$\mathbf{P} = \mathbf{P}_1 \cos (2\pi.\nu t + \theta_1) + \mathbf{P}_2 \cos (2\pi.2\nu t + \theta_2) + \ldots + \mathbf{P}_\tau \cos (2\pi.\tau\nu t + \theta_\tau) + \ldots \qquad (30)$$

In other words, the anharmonic vibration can be resolved into a number of simple harmonic vibrations comprising a fundamental of frequency ν and overtones of frequency 2ν, 3ν . . . $\tau\nu$ . . . The values of the amplitudes $\mathbf{P}_1$, $\mathbf{P}_2$, . . . of the component vibrations determine the actual state of excitation of the oscillator. In classical theory any state of excitation of the oscillator is physically possible, and the oscillator in any state of excitation emits a whole spectrum of frequencies ν, 2ν, 3ν . . . , the intensity of emission of each overtone frequency $\tau\nu$ being proportional to the square of the amplitude $\mathbf{P}_\tau$ of the corresponding Fourier term. In quantum theory, however, the oscillator has a definite physical existence only in a discrete series of states of excitation. Any two of these quantum states may be characterised by their values for the component electric amplitudes $\mathbf{P}_1'$, $\mathbf{P}_2'$, $\mathbf{P}_3'$ . . . and $\mathbf{P}_1''$, $\mathbf{P}_2''$, $\mathbf{P}_3''$ . . ., but they are also characterised by quantum numbers n' and n'' respectively. In either quantum state the oscillator is quiescent, but in transition between them it emits a quantum of monochromatic radiation, the frequency of which is given by the Bohr frequency relation. The Correspondence Principle now states that if this transition involves a change in the quantum number of $(n'' - n') = \tau$ units, the quantum emission process " corresponds " to the classical emission of the overtone frequency

$\tau\nu$, in the sense that the probability of occurrence of the quantum process is determined by the values of $\mathbf{P}_\tau'$ and $\mathbf{P}_\tau''$ which govern the intensities of emission of the overtone frequency $\tau\nu$ in the two combining states in classical theory. When these $\mathbf{P}_\tau$'s are large, the probability of occurrence of the quantum jump for which the quantum number changes by τ units is correspondingly large; when the $\mathbf{P}_\tau$'s are small, the probability of occurrence of the quantum event is correspondingly small. By a Fourier analysis of the motion of the oscillator in each quantum stationary state, the relative probabilities of occurrence of quantum jumps involving changes in the quantum number of 1, 2, 3, 4 . . . units are thus capable of estimation, and these probabilities determine the relative intensities of emission of the monochromatic radiations which accompany these various quantum jumps.

Several important conclusions of a qualitative character result from this Correspondence. In the first place, since the Fourier analysis of the motion of an anharmonic oscillator in any state of excitation involves not only a fundamental but also a whole series of overtone terms, it follows that the anharmonic oscillator can, in general, change its vibration quantum number in spontaneous transitions by any number of units. For the simple harmonic oscillator, however, there are no overtone terms in the Fourier analysis of the motion, which is now simply represented by

$$\mathbf{P} = \mathbf{P}_1 \cos(2\pi\nu t + \theta_1) \quad . \quad . \quad . \quad (31)$$

with a different value of the amplitude $\mathbf{P}_1$ for each state of excitation. Since in this case the $\mathbf{P}_\tau$'s for all values of τ above unity are all equal to zero, it follows that the only quantum transitions permitted to the simple harmonic oscillator are those involving a change in the vibration quantum number of one unit. Accordingly, the Planck oscillator with energy content $nh\nu$ can only alter this energy content by one quantum $h\nu$ at a time, and in doing so can only emit or absorb the frequency ν itself. It cannot emit or absorb the frequencies 2ν, 3ν, 4ν . . . which would be possible, according to Bohr's frequency relation, if changes in n of 2, 3, or 4 units were also permitted.

The circular rotation of an electron about a positive centre of force, or the rotation of a rigid dipole about an axis perpendicular to the dipole axis, is a type of motion which may for analytical purposes be regarded as compounded of two linear, simple harmonic vibrations along two mutually perpendicular axes. For both types of motion, the Correspondence Principle restricts the possible quantum transitions to those involving a change in the quantum number of one unit only. Accordingly, if the motion of the electron in the hydrogen atom were confined to circular orbits, quantum transitions between adjacent orbits would alone be allowed, and the emission spectrum of the atom would contain only the first members

$$\nu = R\left\{\frac{1}{1^2} - \frac{1}{2^2}\right\},\ \nu = R\left\{\frac{1}{2^2} - \frac{1}{3^2}\right\},\ \nu = R\left\{\frac{1}{3^2} - \frac{1}{4^2}\right\} \ldots$$

of the Lyman, Balmer, Paschen, etc. series respectively. The fact that other lines of these series corresponding to changes of n of two, three, four . . . units are also observed is due to the fact that elliptical as well as circular orbits are possible for the rotating electron. Motion in an elliptic orbit involves two degrees of freedom and requires for its description two independent quantum numbers n and k. A detailed analysis of this type of motion in terms of the Correspondence Principle now indicates that the electron in quantum transitions between stationary orbits, whether elliptical or circular, can alter its principal quantum number n by any number of units, but can only increase or decrease its azimuthal quantum number k by one unit. Actually, the result of this restriction so far as the series spectrum of hydrogen is concerned is obscured by the circumstance that in this special case electron orbits with the same value of n but different values of k are practically identical energetically. This is not so, however, for the more general atom model which is represented by an optical electron revolving in a rosette path under the influence of a central but non-Coulomb field of force. In this case, orbits with the same n but different k's differ in respect of their energy contents, and on this account we have the S, P, D, F . . . sequences of spectral terms. Here also, however, the Correspondence Principle requires that the azimuthal quantum number k should only increase or decrease by one unit, and in agreement with this we have the empirical result already stated that the $S(k = 1)$ terms combine only with $P(k = 2)$ terms, the P terms only with S and with $D(k = 3)$ terms, and the D terms only with P and with $F(k = 4)$ terms.

Before ending this brief statement of the Correspondence Principle, it should be pointed out that the restrictions which it imposes are only meant to apply to quantum transitions which involve the simultaneous emission or absorption of radiation. The Principle has nothing to say regarding the possibility or probability of occurrence of "radiationless" quantum jumps such as might be effected through the agency of collisions. Also the Principle breaks down when the radiating or absorbing system is subject to the influence of strong electric or magnetic fields. Under such circumstances, for example, the emission or absorption of spectral lines involving "forbidden" combinations of terms, such as $S - S$ or $S - D$ combinations, is often possible. Transition probabilities are further discussed in the next Chapter.

The Principal Quantum Numbers of Spectral Terms.—Having distinguished the S, P, D, F . . . sequences of terms from which the lines of a series spectrum are built up by the different values of the azimuthal quantum number k to which they correspond, there remains to be discussed the possibility of assigning the principal quantum number to each spectral term. In this connection, it must first be emphasised that, although the consecutive numbers of a sequence of spectral terms correspond in all probability to electronic orbits the principal quantum numbers of which differ by unity, there is no *a priori* justification for identifying the empirical serial number n of any term, say the nP term, with the principal quantum number of that term. For S and P terms, at least, no such agreement exists in actual fact. We must, therefore, distinguish clearly between (1) the empirical serial number n of a spectral term, (2) the effective total quantum number n^*, which, being defined by writing the value of the term in the form RZ^2/n^{*2}, is not in general an integer, and (3) the true principal quantum number n of the term. Similarly we must not confuse the apparent Rydberg correction, say P, which occurs in the empirical mode of expression of the term, viz. $\frac{RZ^2}{(\mathrm{n} + P)^2}$, with the true Rydberg correction δ which enters with the principal quantum number n in the term expression $\frac{RZ^2}{(n + \delta)^2}$. We have

$$n^* = \mathrm{n} + P = n + \delta, \qquad . \quad . \quad . \quad (32)$$

but the actual values of n and P are empirical since n is an arbitrarily chosen serial number.

A preliminary guide to the evaluation of the true principal quantum numbers of the terms is obtained by the following argument. For our hypothetical atom model of page 71, the energy of the system when the electron is in any n_k orbit is given by

$$-W_n = -\frac{RhZ^2}{(n + \delta)^2} = -\frac{RhZ^2}{n^{*2}} \qquad . \quad . \quad . \quad (33)$$

If the deviation of the central field from the Coulomb Law is small at all points in the electron's path, then, as already stated, the true Rydberg correction δ is a small *negative* quantity which is independent of n but varies inversely with some power of k. For large values of k, that is, for the D and especially for the F terms, the true Rydberg correction δ must be almost negligible, and therefore the principal quantum number n cannot differ greatly from the effective quantum number n^* of the term. Actually it is found for the F spectral terms of nearly all the elements which give line series spectra, and to a lesser extent also for the D terms, that the effective total quantum numbers n^* differ very little indeed from whole numbers, such difference as there is being always in the sense that the effective quantum number is *slightly less* than a whole number. We are justified then in identifying the integers nearest to the n^*'s with the principal quantum numbers of the D and F terms.

On the other hand, for the orbits corresponding to the S and P terms ($k = 1$ and $k = 2$ respectively), the radiating electron must approach very close to or even penetrate the atom residue over a part of its orbit. For such orbits, theory shows that δ should be a much larger negative quantity, not dependent solely upon k, but also upon n. We shall find it convenient to speak of the "negative Rydberg correction," meaning the value of $-\delta$ or $|\delta|$. If now we compare orbits of different total quantum numbers but the same azimuthal quantum number, it is easy to see that the larger the value of n, the more of the orbit should be situated in the outer Coulomb part of the field, and accordingly the smaller the true negative Rydberg correction should become. In the limit of large values of n, $|\delta|$ should become independent of n and dependent only on k, being the smaller the larger k is. Corresponding to these predictions, we have the experimental facts that (*a*) the effective quantum numbers n^* of the S and P spectral terms do not usually approximate to whole numbers as do the n^*'s of D and F terms, in other words, the decimal parts of the apparent Rydberg corrections S and P differ appreciably from 0 or 1; and (*b*) the apparent Rydberg correction in an S or a P sequence is not really a constant, but its value often changes very appreciably from term to term of a sequence, approaching constancy only for large serial numbers n of the term. For this last reason, the values of the terms in an S sequence are very often represented more accurately by one or other of the Ritz Formulæ—

$$\nu_S = \frac{RZ^2}{\left(\mathrm{n} + S + \frac{\alpha}{\mathrm{n}^2}\right)^2}, \text{ or } \nu_S = \frac{RZ^2}{(\mathrm{n} + S + \beta\nu_S)^2},$$

than by the Rydberg expression $\nu_S = \frac{RZ^2}{(\mathrm{n} + S)^2}$, and similarly also for a P sequence of terms.

Now the apparent Rydberg correction for any term may be positive or negative depending upon the value of the arbitrary serial number which is assigned to the term. The true Rydberg correction, however, must be negative, and we can always determine the decimal part of its value from the apparent Rydberg correction or the effective quantum number by use of the relation

$$n^* = \mathrm{n} + S = n + \delta_S$$

or

$$n^* = \mathrm{n} + P = n + \delta_P, \text{ etc.}$$

Thus, the effective quantum number of the first (1S) term in the sequence of the sodium arc spectrum equals 1·63 (cf. Table II.). The apparent Rydberg correction is, therefore, + 0·63. The true Rydberg correction for this term, however, must be either − 0·37 or − 1·37 or − 2·37, etc., and correspondingly the true principal quantum number of the 1S term of sodium must be either 2 or 3 or 4, etc. We now introduce the condition that the limiting values (for large serial numbers) of the negative Rydberg corrections $-\delta_S$, $-\delta_P$, $-\delta_D$, and $-\delta_F$ for any series spectrum must progressively decrease in value in the order given, and δ_F at least must be practically zero. It follows from this that if we prefix to the known decimal parts of the limiting $-\delta$'s the smallest integers which will make the above condition valid, we shall obtain the *least possible values* of the limiting negative Rydberg corrections, and from these we can then deduce the least possible values of the principal quantum numbers of the terms.

As an example of the application of this principle, we may consider in detail the case of the arc spectrum of sodium. In Table II. we give the values (experimental) of the effective total quantum numbers of the first few terms in the *S*, *P*, *D*, and *F* sequences. The terms are numbered in the table in accordance with the empirical scheme given in Chapter I. Actually, of course, the *P*, *D*, and *F* terms of this spectrum are multiplets, but for the present purpose this may be ignored, since the components of each multiplet term are so close that the choice of component does not materially affect the value of n^*. It should first be noted from the table that, whereas the effective quantum numbers of the *D* and *F* terms are practically integral, the n^*'s of the *S* and *P* terms are not so by any means. Again, in the *S* and *P* sequences the apparent Rydberg corrections are not quite constants, but increase slightly over the first few members of each sequence in the manner already indicated. With our empirical numbering of the terms, the sequence " constants " *S*, *P*, *D*, and *F* assume the limiting values given in the first row of Table III. (*a*). From these we readily obtain the decimal parts of the limiting negative Rydberg corrections (second row), and the *minimal values* of the limiting negative Rydberg corrections are then derived by prefixing appropriate units to these decimals as in the last row of the table.

TABLE II.

EFFECTIVE QUANTUM NUMBERS n^* OF THE FIRST FEW *S*, *P*, *D*, AND *F* TERMS OF Na.

S sequence .	1*S* 1·63	2*S* 2·64	3*S* 3·65	4*S* 4·65	5*S* 5·65
P sequence .	—	2*P* 2·12	3*P* 3·13	4*P* 4·14	5*P* 5·14
D sequence .	—	—	3*D* 2·99	4*D* 3·99	5*D* 4·99
F sequence .	—	—	—	4*F* 4·00	5*F* 5·00

If now these minimal values are the actual values of the limiting negative Rydberg corrections in the different sequences, then the principal quantum numbers of the higher terms in each sequence, and hence of all the terms in the arc spectrum of sodium, can easily be deduced. Thus for the fourth term in the *P* sequence $n^* = 5{\cdot}14$. If $\delta = -0{\cdot}86$, then since $n^* = n + \delta$, the principal quantum number n must be 6, and, counting back, the principal quantum number of the first (2*P*) term in the sequence must be 3. Similar calculations for the other sequences results in the following scheme of principal and azimuthal quantum numbers for the entire system of terms in the arc spectrum of sodium :—

S sequence	3_1	4_1	5_1	6_1 . . .
P sequence	3_2	4_2	5_2	6_2 . . .
D sequence	3_3	4_3	5_3	6_3 . . .
F sequence	—	4_4	5_4	6_4 . . .

These predicted values are indeed the correct ones, as borne out by independent evidence, but it must be emphasised that this is not a logical necessity and that the above reasoning claims only to set a lower limit to the principal quantum numbers of the terms, not to determine their actual values without ambiguity. We can illustrate the limitations of the method by reference to the case of the arc spectrum of rubidium. For the terms of this spectrum, the limiting values of the sequence " constants," the decimal parts of the limiting negative Rydberg corrections, and the minimal values of these same corrections are given in Table III. (*b*). Taking the *S* sequence of terms, the minimal value of $|\delta|$ for the higher members of the sequence is 1·13. If this represents its actual value, then for any (higher) n*S* term, we have the following relation between the serial number n and the principal quantum number *n* :—

TABLE III.

(*a*) Arc Spectrum of Sodium.

Sequence.	*S.*	*P.*	*D.*	*F.*
Limiting value of sequence " constant " . .	+ 0·65	+ 0·14	− 0·01	+ 0·00
Decimal part of − δ .	+ 0·35	+ 0·86	+ 0·01	+ 0·00
Minimal value of − δ .	+ 1·35	+ 0·86	+ 0·01	+ 0·00

(*b*) Arc Spectrum of Rubidium.

Sequence.	*S.*	*P.*	*D.*	*F.*
Limiting value of sequence " constant " . .	+ 0·87	+ 0·34	− 0·35	− 0·03
Decimal part of − δ .	+ 0·13	+ 0·66	+ 0·35	+ 0·03
Minimal value of − δ .	+ 1·13	+ 0·66	+ 0·35	+ 0·03

$$\mathrm{n} + P = n + \delta\,;\ \text{i.e. } \mathrm{n} + 0{\cdot}87 = n - 1{\cdot}13\,;\ \text{i.e. } n = \mathrm{n} + 2.$$

Counting back, the principal quantum number of the first term (1*S*) of the sequence should then be equal to 3. A similar calculation for the *P* terms suggests the value 3 for the principal quantum number of the first ($2P$) term. We should be misled, however, in the case of rubidium if we took these to represent the actual principal quantum numbers of the first S and P terms. The true value of n is 5 in each case, and the true negative Rydberg corrections differ correspondingly by two units from the minimal values given in the table. The correct values of the $-\delta$'s, viz.

TABLE IV.

Element.	Quantum Numbers (n_k) of First Term.				Effective Quantum Numbers (n^*) of First Term.			
	S.	P.	D.	F.	S.	P.	D.	F.
H	$\mathbf{1_1}$	2_2	3_3	4_4	1·00	2·00	3·00	4·00
He	$\mathbf{1_1}$	2_2	3_3	4_4	0·74	2·01	3·00	4·00
Li	$\mathbf{2_1}$	2_2	3_3	4_4	1·59	1·96	3·00	4·00
O	3_1	$\mathbf{2_2}$	3_3	4_4	1·82	1·00	2·98	—
Ne	3_1	$\mathbf{2_2}$	3_3	4_4	1·66	0·79	2·97	—
Na	$\mathbf{3_1}$	3_2	3_3	4_4	1·63	2·12	2·99	4·00
Mg	$\mathbf{3_1}$	3_2	3_3	4_4	1·33	2·03	2·68	3·96
Al	4_1	$\mathbf{3_2}$	3_3	4_4	2·19	1·51	2·63	3·97
K	$\mathbf{4_1}$	4_2	3_3	4_4	1·77	2·23	2·85	3·99
Ca	$\mathbf{4_1}$	4_2	3_3	4_4	1·49	2·07	2·00	3·97
Cu	$\mathbf{4_1}$	4_2	3_3	4_4	1·33	1·86	2·98	4·00
Zn	$\mathbf{4_1}$	4_2	3_3	4_4	1·20	1·94	2·87	3·98
Ga	5_1	$\mathbf{4_2}$	3_3	—	2·16	1·51	2·84	—
Rb	$\mathbf{5_1}$	5_2	3_3	4_4	1·80	2·27	2·77	3·99
Sr	$\mathbf{5_1}$	5_2	4_3	4_4	1·54	2·13	2·06	4·14
Ag	$\mathbf{5_1}$	5_2	3_3	4_4	1·34	1·87	2·98	3·99
Cd	$\mathbf{5_1}$	5_2	3_3	4_4	1·23	1·95	2·87	3·97
In	6_1	$\mathbf{5_2}$	3_3	—	2·21	1·53	2·82	—
Cs	$\mathbf{6_1}$	6_2	3_3	4_4	1·87	2·35	2·55	3·98
Ba	$\mathbf{6_1}$	6_2	5_3	4_4	1·62	2·14	1·89	2·85
Au	$\mathbf{6_1}$	6_2	3_3	—	1·21	1·72	2·98	—
Hg	$\mathbf{6_1}$	6_2	3_3	4_4	1·14	1·91	2·92	3·97
Tl	7_1	$\mathbf{6_2}$	3_3	4_4	2·19	1·49	2·89	3·97

$$3{\cdot}13,\ 2{\cdot}66,\ 0{\cdot}35,\ \text{and}\ 0{\cdot}03,$$

still conform, of course, to the condition that they should decrease in the order given.

Besides the above method which serves to give minimal values to the negative Rydberg corrections of spectral terms, there are other methods by which rough estimates of their absolute values may be obtained. One of these involves a comparison of the spatial dimensions of the atom residue (in the field of which the radiating electron revolves) with the dimensions of the different possible orbits of the radiating electron. Even for the lightest atoms it is found that the electron moving in an $S(k = 1)$ orbit must actually penetrate the atom residue over part of its path. For the heavier atoms the $P(k = 2)$ orbits can also penetrate the atom residue. By computing the extent of penetration of any particular orbit of the radiating electron it is possible to obtain an approximate value for the Rydberg correction of the corresponding spectral term. Without entering into details, it may be said that as a result of such considerations the true Rydberg corrections and the true principal quantum numbers of the optical terms of the elements are now known with few exceptions. Table IV. contains the values of the true principal and azimuthal quantum numbers and also the effective quantum numbers of the first (largest) terms of each S, P, D, and F sequence for a few of the elements—chiefly elements belonging to the first three groups of the Periodic Classification. In each case, the term which is numerically the largest of all, and which, therefore, corresponds to the normal orbit of the radiating electron, is printed in heavier type. This is, of course, the term for which the effective quantum number is least. It will be noted that for all atoms belonging to a homologous series, such as Li, Na, K, Rb, and Cs, or Mg, Ca, Sr, and Ba, the type (azimuthal quantum number) of the orbit occupied by the radiating electron in its normal state is always the same, but the principal quantum number of the orbit progressively increases by one unit as we go up the homologous series. This fact is important in relation to our present views (cf. p. 106) on the disposition of the totality of the extra-nuclear electrons of any atom about the nucleus.

X-RAY SPECTRA.

All modern theories of the atom agree in supposing that the electron atmosphere which surrounds the nucleus consists of a few outer (valency) electrons loosely bound to the atom and one or more inner groups of firmly bound electrons which for the heavier atoms comprise the major part of the electron atmosphere. The number and binding of the peripheral valency electrons determine the chemical properties of the atom, and their reactions with radiation are evidenced in its optical series spectrum. This type of spectrum is characteristic of the atomic state, for when the valency electrons are engaged in chemical combination their orbits and strength of binding are considerably modified and the optical spectrum of the compound is a band spectrum which usually possesses no features in common with the series spectra of the constituent atoms. On the other hand, atoms and molecules alike react with radiation of very high frequencies to give *X*-ray emission and absorption spectra, and the characteristic *X*-ray spectrum of any element is exactly the same whether the element is in the atomic or the molecular state or is held in chemical combination with other elements. For this reason it is presumed that in the emission and absorption of X-rays by matter, only the internal non-valency electrons of the atom are concerned. These being much more firmly bound than the peripheral electrons, it is natural that the energy quanta concerned in X-ray emission or absorption should be hundreds or thousands of times greater than the quanta involved in the optical range of frequencies.

X-Ray Absorption Edges.—We will consider first of all the X-ray absorption spectra of the elements, since these are of more direct theoretical significance than their X-ray emission spectra. Apart from the difference in the frequency ranges involved, the X-ray absorption spectrum of an atom is quite different in its main characteristics from the optical absorption spectrum. The latter is essentially a line series, and represents the reversal of one of the line series in the optical emission series of the element. The X-ray absorption spectrum consists, however, not of lines but of a number of continuous bands, each band beginning sharply and with a maximum of absorption at a long wavelength limit or edge and fading away more or less gradually on the short wave-length side. Beginning with the band of greatest frequency, these sharp absorption edges are distinguished by the symbols $K, L, M, N. \ldots$

Now the frequencies of corresponding absorption edges for the different elements exhibit a very simple and suggestive dependence upon their atomic numbers. The frequencies of the $K, L, M \ldots$ absorption edges are in fact given to a first approximation by

$$\nu_K = \frac{R(Z - z_1)^2}{1^2},\ \nu_L = \frac{R(Z - z_2)^2}{2^2},\ \nu_M = \frac{R(Z - z_3)^2}{3^2}, \text{ etc.} \qquad (34)$$

Here R is the familiar Rydberg constant, Z is the atomic number of the element and $z_1, z_2, z_3 \ldots$ are small constants increasing in the order given, the meaning of which will appear presently. Actually, the plots of $\sqrt{\nu_K}, \sqrt{\nu_L}, \sqrt{\nu_M} \ldots$ against Z are not strictly linear in practice as demanded by the above relations, but are slightly convex to the Z axis. The deviations from linearity may, however, be taken account of by allowing the "constants" $z_1, z_2, z_3 \ldots$ to vary slightly from element to element.

The above functions for $\nu_K, \nu_L, \nu_M \ldots$ are very similar as regards their form to the convergence limits $\nu = \frac{R'}{1^2}, \frac{R}{2^2}, \frac{R}{3^2} \ldots$ of the Lyman, Balmer, Paschen . . . series of hydrogen. Further, the regions of continuous absorption appended to each X-ray absorption edge are strongly reminiscent of the regions of continuous absorption which should in theory be appended to the convergence positions of these hydrogen series in absorption (it may be recalled that such a region of continuous absorption attaching to the convergence limit of the Balmer series has been experimentally observed). These regions of continuous absorption in the optical case correspond to the complete ionisation of the hydrogen atom by the removal of its valency electron to infinity, and it appears certain that the continuous absorption bands in the X-ray spectrum of any element must similarly be associated with the complete removal of electrons from various stationary orbits in the interior of the atom. On this view the quantum absorbed at the K absorption edge is just sufficient to cause the ejection of one of the innermost electrons, revolving in a $n = 1$ orbit, out of the atom. The absorption of a quantum of radiation of any higher frequency effects the same physical process, the excess energy appearing as energy of translatory motion of the ejected electron. Again, the quantum corresponding to the L absorption edge also suffices to liberate an inner ($n = 2$) electron, and since the L absorption edge has a smaller frequency than the K edge this electron must be one which is not so firmly held in the atom as the first mentioned. Similar meanings can obviously be attached to the M, N . . . absorption edges. Finally, the absence of series absorption lines in the X-ray absorption spectrum leading up to the continuous regions of absorption as in the optical analogue must be taken to mean that, in the atom which absorbs a quantum of X-ray radiation, there are no possible stationary states for the electron which is ejected, intermediate between its normal stationary state inside the atom and that which corresponds to its complete ejection. The successive quantum orbits between the nucleus and the periphery of the atom into which the ejected electron might pass must in the normal atom be already occupied by electrons.

Since the total number of electrons in the electron atmosphere of any atom is equal to the atomic number of the element, it is clear that for the heavier atoms a large number of electrons have to be disposed of in some way inside the valency shell. There are, however, even for the heaviest elements, only a limited number of X-ray absorption edges. We must therefore imagine that the totality of internal electrons in any atom are divided up into a few groups, the K, L, M . . . groups of electrons, which groups are characterised by the principal quantum numbers $n = 1, 2, 3$ . . . for the orbits of the electrons which they comprise. The K absorption edge then results from the complete ejection from the atom of any one of the $K(n = 1)$ group of electrons, the L absorption edge from the complete ejection of any one of the $L(n = 2)$ group, etc. All the electrons belonging to the same main group may for the moment be regarded as similarly bound in the atom, either sharing the same orbit to form a rotating K, L, or M ring of electrons about the nucleus, or occupying separate but similar orbits which are symmetrically arranged in space about the nucleus.

The above allocation of principal quantum numbers to the successive K, L, M . . . groups of inner electrons may be justified, and at the same time the nature of the terms z_1, z_2, z_3 . . . used in equations (34) may be made clear, by the following argument. In atoms of large atomic number any electron in an innermost orbit is acted upon partly by the attraction of the positive nucleus of charge Ze and partly by the forces of repulsion of all the other extra-nuclear electrons in the system. If all or most of these electrons occupy orbits external to that of the electron considered, and if in addition these orbits are more or less symmetrically disposed within the atom, their individual effects upon the innermost electron will compound roughly into a small force of repulsion, acting from the position of the nucleus and having the effect of diminishing slightly the net central force of attraction. If then the principal quantum number of the innermost electron's orbit is n_1, its energy is given by

$$-W_1 = -\frac{Rh(Z-s_1)^2}{{n_1}^2},$$

where $(Z - s_1)$ is but slightly less than Z. The quantity s_1 is termed the "screening constant" for the innermost shell of electrons. The value of W_1 itself represents the amount of energy required to remove the innermost electron completely from its orbit and eject it to infinity, leaving the rest of the system unaltered. Again, for any electron in the second (L) shell within the atom, the effective central positive charge which determines the field in which it moves must be appreciably less than the nuclear charge itself. On the one hand, the electrons of the innermost group all contribute to screen the electron from the central force of attraction of the nucleus; on the other hand, the forces of repulsion from electrons in the same shell and in outer shells will probably compensate one another less completely. These factors can be taken account of roughly by again assuming the nuclear charge reduced, but in this case by a screening constant s_2 where $s_2 > s_1$. If the principal quantum number of the L electron's orbit is n_2, its energy is then given by

$$-W_2 = -\frac{Rh(Z-s_2)^2}{{n_2}^2}$$

A similar form of expression

$$-W_3 = -\frac{Rh(Z-s_3)^2}{{n_3}^2}$$

can be written for the energy of any electron in the M group, with $s_3 > s_2$.

Now the positive quantities $W_1, W_2, W_3 \ldots$ represent the energies required for the complete ejection from the atom of an electron belonging to each of the groups indicated. On the basis of our interpretation of the X-ray absorption edges, however, these energies, when divided by h, should give the frequencies of the $K, L, M \ldots$ absorption edges. For formal agreement of these values with the $\nu_K, \nu_L, \nu_M \ldots$ of equations (34) it is only necessary that the quantum numbers n_1, $n_2, n_3 \ldots$ of the orbits of electrons in successive shells inside the atom should have the values 1, 2, 3 . . . respectively, and that the empirical constants $z_1, z_2, z_3 \ldots$ of equations (34) should be identified with the screening constants $s_1, s_2, s_3 \ldots$ of the different shells.

We see from the above that the various energy levels within any atom are given quantitatively by the frequencies of its X-ray absorption edges. These frequencies are to be regarded as the true X-ray spectral terms, analogous in meaning to the optical spectral terms of the atom. At this stage we may now consider the X-ray emission spectra of the elements.

X-Ray Emission Spectra.—The normal method of generating X-rays is to bombard an anticathode of some suitable material with high-speed cathode rays. For sufficiently high velocities of the cathode rays, an emission is obtained from the anticathode which consists partly of a continuous X-ray spectrum, partly of a superimposed line spectrum. The nature of the continuous emission depends only to a subsidiary extent on the material of the anticathode. The line spectrum, however, is highly specific, and is termed the characteristic X-ray spectrum of the substance in question. The various lines of this characteristic X-ray spectrum of an element group themselves naturally into different series, known as the K, L, M, N . . . series, which usually lie in well-separated spectral regions. The lines of the K series have always the greatest frequencies, the L series comes next in order, the M series next, and so on. Normally each series contains only a few lines, but each line may possess a multiplet structure just as do the lines in optical series spectra. Ignoring for the present this fine structure, the first lines (in order of increasing frequency) of the K series are denoted by K_α, K_β, K_γ . . ., the first lines of the L series by L_α, L_β, L_γ . . ., etc.

The characteristic X-ray emission spectrum of an element can be generated not only by cathode ray bombardment but also as a fluorescence by illumination of the material with X-rays of suitable frequency. The exact nature of the emission produced in this way depends upon the hardness (frequency) of the exciting radiation. If the exciting beam contains frequencies greater than that of the K absorption edge of the element, the complete X-ray spectrum—K, L, M . . . series—is emitted. If, however, the incident beam contains frequencies above that of the L absorption edge but below that of the K edge, the K series of lines is completely absent from the fluorescence, which now contains only the L, M, N . . . series of lines. It follows from this that the emission of the K series of lines is conditioned by the preliminary ejection of an electron from the K shell within the atom. The emission of the L series may, however, result from the ejection of an electron either from the K or from the L shell.

From the different characters of the X-ray emission and absorption spectra of any element, the two spectra are clearly not reciprocal in the same sense as are optical emission and absorption spectra. Nevertheless the relationship in which they stand to one another is very simple. Each X-ray emission frequency is found to be capable of expression as the difference of the frequencies of two X-ray absorption edges of the same element. Thus—

$$K_\alpha = \nu_K - \nu_L;\quad K_\beta = \nu_K - \nu_M;\quad K_\gamma = \nu_K - \nu_N;$$
$$L_\alpha = \nu_L - \nu_M;\quad L_\beta = \nu_L - \nu_N;\quad L_\gamma = \nu_L - \nu_O;\ \text{etc.}$$

Each X-ray line is thus expressed as the difference of two X-ray terms and, as seen above, each of these terms represents the energy required for the complete ejection of an electron from some shell within the atom. The X-ray emission line must therefore be supposed to originate as follows. Whether the emission be excited by absorption of X-rays or by collision of the atom with a high-speed cathode ray, the primary process consists of the ejection of an electron from some part of the extra-nuclear structure. The resulting system, being no longer stable, strives to regain its internal stability by replacing an electron in the vacated position. The electron used to this end cannot, however, be that which was originally ejected or any other electron free in space. If it were, the readjustment would simply constitute a reversal of the primary process, and the frequency of the emission would necessarily lie within one or other of the continuous X-ray absorption bands. The frequency actually emitted, however, whether it be a K, L, or M line, is definitely lower than the frequency of the corresponding absorption edge. We are therefore forced to conclude that the electron

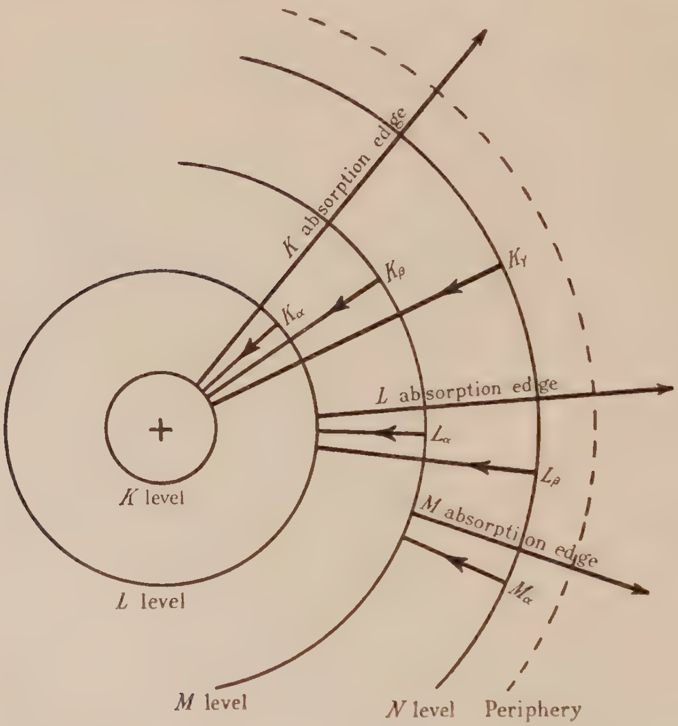

FIG. 12.—Illustrating X-ray emission and absorption.

which is drawn into the vacated position comes, not from outside the atom, but from one or other of the groups of electrons external to the group concerned in the original act of absorption. The quantum of energy released in this process would be equal to the difference in the energies required to remove an electron completely from the two combining shells, which is in agreement with the essential term structure of each X-ray emission line. If in the primary process of excitation an innermost K electron is ejected from the atom, the vacated position is subsequently filled by an electron taken from the L or M or N shell, and, depending upon which of these latter shells is involved, the K_α or K_β or K_γ line of the X-ray spectrum is emitted. If the L group of electrons is robbed of an electron to restore the balance in the first group, the K_α line is emitted. The L group is, however, now incomplete, so that an electron in a group still further removed from the nucleus is now drawn into this L group with emission of one or other line of the L series, and these consecutive adjustments must go on until finally the last made vacancy in the outermost (valency) group of electrons is filled by the capture of a free electron. Alternatively, however, the emission lines of the L, M, N . . . series can also be produced if the electron originally ejected by absorption or by collision with a cathode ray comes from the second, third, or fourth group within the atom. The genesis of various X-ray emission lines and the relationship of the two processes of emission and absorption can easily be followed from the diagram of Fig. 12. In this diagram, the various internal groups of electrons are for convenience represented by concentric rings about the nucleus.

Multiplicity of X-Ray Spectral Terms.—So far we have discussed the X-ray terms and energy levels within the atom only in regard to the principal quantum numbers of the electronic orbits concerned, and correspondingly we have ignored the fine structure which is actually observed, not only for the X-ray emission lines, but also for the absorption edges. The two first and predominant lines K_α and K_β of the K series of the higher elements are found to be really two close doublets, labelled K_{α_2}, K_{α_1} and K_{β_2}, K_{β_1} respectively in order of increasing frequency. The various members of the L series of the higher elements are also doublets, though in their case the doublet structure is not at first sight so obvious since the components of the different pairs are to some extent intermingled. That the L series is primarily a series of doublets is, however, made clear by the fact that, when the components are properly associated, the resulting doublets exhibit a constant frequency separation which is, moreover, identical in value with the frequency separation

$$\Delta\nu = \nu_{K_{\alpha_1}} - \nu_{K_{\alpha_2}}$$

of the two components of the K_α emission line of the same element. For the heavier elements as many as five of these associated pairs, the so-called "relativity doublets" of the X-ray spectrum, are found in each L emission series. The magnitude of $\Delta\nu$ increases rapidly with increasing atomic number of the element. To a fair approximation, the fourth root of $\Delta\nu$ varies linearly with Z, viz.

$$\Delta\nu = a(Z - s)^4,$$

where a and s are constants. The latter is practically the same in value as the screening constant z_2 of the L group of electrons within the atom. Besides the two main components of each member of the L series which form the relativity doublet, there are other apparently unassociated components. We need not at the moment consider these or the complexity of lines in the M, N . . . series in any more detail.

The multiplicity of X-ray emission lines must finally be referred to a multiplicity in the system of combining X-ray terms, so that we may more profitably consider the absorption edges which give these terms directly. It is found that for each element, whatever its atomic weight may be, there is one and only one K absorption edge. Hence for each element there is a single X-ray term of principal quantum number $n = 1$. Referring to our previous concepts of electronic orbits, this singlet K term must be associated with an electron inside the atom which revolves in a practically circular ($n = 1$, $k = 1$) orbit. No other value of k, consonant with $n = 1$, is possible, since k cannot exceed n and $k = 0$ is forbidden because it would correspond to a linear vibration of the electron through the centre of force—the nucleus. We may conclude from this that there is only one type of orbit, viz. the 1_1 orbit, represented in the K group of electrons in any atom.

Turning now to the L group, it is found that for each of the lighter elements there is actually or apparently only one L absorption edge. As the atomic number of the element increases, however, a doublet structure of the L edge emerges, the separation of the two components L_{II} and L_{III} increasing rapidly with increasing atomic number. Moreover, for elements of atomic number greater than 40, a third component L_I enters, the frequency of which is greater than that of either L_{II} or L_{III}. The two absorption edges L_{II} and L_{III} form a "relativity doublet," since their separation ($\nu_{L_{II}} - \nu_{L_{III}}$) for any element is identical in value with that of the "relativity doublets" of the K_α emission line and of the various L emission lines of the same element. The separation of the L_I and L_{II} absorption edges which form a "screening doublet" is different in value from this. Unlike the relativity doublet, the screening doublet never occurs in emission, in other words, any X-ray level which combines with the L_{II} level never combines also with the L_I level. The relationship between the three L absorption edges of the various chemical elements is shown by the curves L_I, L_{II}, L_{III} of Fig. 13, which represent the values of $\sqrt{\frac{\nu}{R}}$ plotted against Z. Those elements which exhibit three different L absorption edges presumably have three different L energy levels, three different L

terms, and three different L sub-groups of internal electrons.* Apparently, however, the L_{I} sub-group of electrons is only present in the

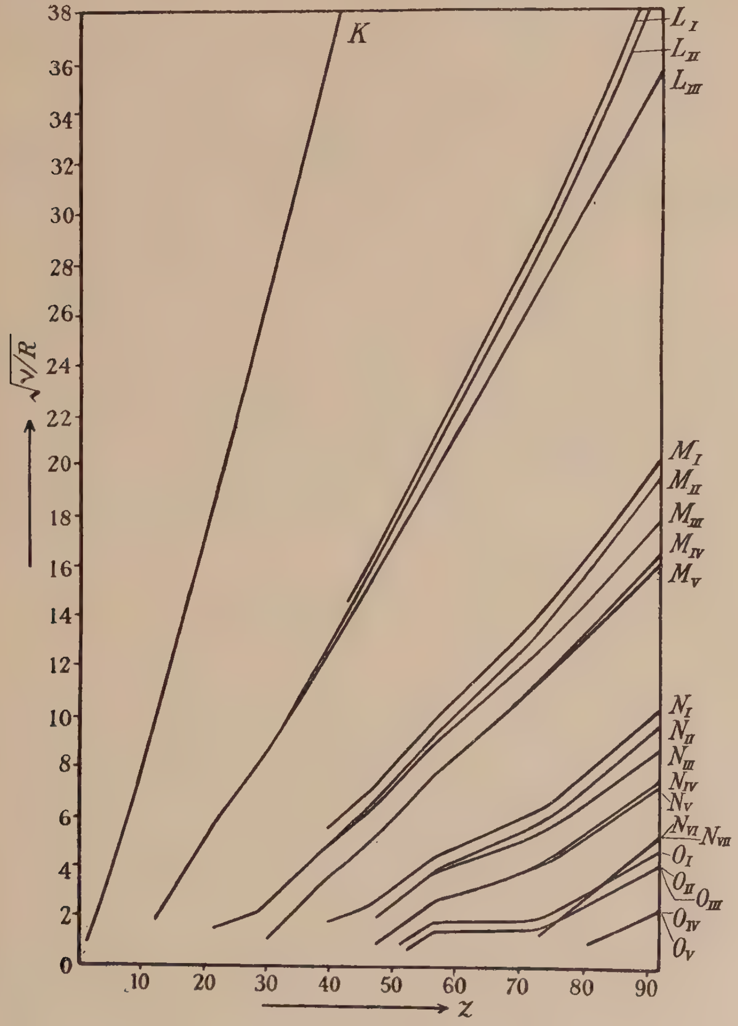

Fig. 13.—Plot of $\sqrt{\nu/R}$ for X-ray terms against atomic number.

elements of atomic number above 40, since the L_{I} absorption edge enters abruptly here, instead of separating gradually from either of the other edges. On the other hand, the nature of the L_{II} and L_{III} curves suggests that all the elements of atomic number between 10 and 40 contain both types L_{II} and L_{III} of internal electrons, although for the elements of atomic number less than 30 the two types are not distinguishable energetically.

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* See, however, p. 104.

We must now decide wherein lies the difference between the electronic orbits which characterise the three L sub-groups of electrons. It has already been indicated that all the electrons in the main L group of any atom move in orbits of principal quantum number $n = 2$. There are, however, in the n_k classification of orbits, only two different types of orbits for which $n = 2$, namely, orbits with azimuthal quantum number $k = 1$ and orbits with azimuthal quantum number $k = 2$. From this it is at once evident that a complete differentiation of the three L sub-groups in terms of the possible values of k is not feasible. It is nevertheless desirable to obtain the k values of the different types of orbits, even though two at least of the three types must belong to the same category. The correct allocation of the k's is readily effected by applying the Selection Principle $\Delta k = \pm 1$ to the observed combinations of the partial L terms with the singlet K term in emission. The X-ray terms $\nu_{L_{II}}$ and $\nu_{L_{III}}$ both combine with the term ν_K to give the K_α doublet in the X-ray emission spectrum, but no X-ray emission line is observed which would correspond to the term combination $(\nu_K - \nu_{L_I})$. Since the azimuthal quantum number of the ν_K term is unity, the azimuthal quantum numbers of the three L terms must then be as follows :—

$$\begin{array}{c} L_I \\ k = 1 \end{array} \qquad \qquad \underbrace{L_{II} \qquad L_{III}}_{k = 2}.$$

It appears from this that it is the L_{II} and L_{III} sub-groups of electrons which are not separately distinguishable by use of the n_k system of nomenclature of electronic orbits. These two sub-groups are, however, different energetically, so that the necessity for some extension of our mode of classifying electronic orbits is herewith indicated.

The same necessity is apparent from a study of the multiplet structure of the M and N absorption edges or terms. The M group of internal electrons are those occupying orbits of principal quantum number $n = 3$, and on the simple n_k classification these should subdivide into three groups $n_k = 3_1$, $n_k = 3_2$, and $n_k = 3_3$, with three corresponding M absorption edges for each element. A glance at Fig. 13 shows, however, that for elements of atomic number above 40, at least *four* M absorption edges can be identified, and in the X-ray absorption and emission spectra of the heaviest elements there are altogether *five different* M *absorption edges or terms.* Of these five terms, four group themselves into a pair of " relativity doublets " $(M_{II} - M_{III})$ and $(M_{IV} - M_V)$, while the remaining term M_I forms with M_{II} " a screening doublet " of the same type as the $(L_I - L_{II})$ screening doublet. The combination $(M_{III} - M_{IV})$ may also be regarded as forming another screening doublet.

When the Selection Principle $\Delta k = \pm 1$ is applied to the observed combinations (in emission) of M terms with L and K terms, it is found that the five M terms group themselves in regard to the values of their azimuthal quantum numbers as follows :—

$$\underset{k=1}{M_{\mathrm{I}}} \qquad \underbrace{M_{\mathrm{II}} \quad M_{\mathrm{III}}}_{k=2} \qquad \underbrace{M_{\mathrm{IV}} \quad M_{\mathrm{V}}}_{k=3}.$$

Again, for the heaviest elements it is possible to distinguish in all *seven different N terms* for each of which the principal quantum number $n = 4$, and the azimuthal quantum numbers of which are given by :—

$$\underset{k=1}{N_{\mathrm{I}}} \quad \underbrace{N_{\mathrm{II}} \quad N_{\mathrm{III}}}_{k=2} \qquad \underbrace{N_{\mathrm{IV}} \quad N_{\mathrm{V}}}_{k=3} \qquad \underbrace{N_{\mathrm{VI}} \quad N_{\mathrm{VII}}}_{k=4}.$$

Working by analogy we should expect the total number of O terms to be nine and of P terms to be eleven, but actually there are only five O terms and three P terms, and these are only observed or inferred for the very heaviest elements. We have every reason to believe that several electrons of the atom's atmosphere are associated with each internal energy level, so that for the lightest elements there are only K and L levels, whereas for elements of atomic number above 20 one or more M sub-groups of electrons form an integral part of the extra-nuclear structure, and when the atomic number 40 is reached the N sub-groups of electrons begin to emerge. It may readily be surmised then that even for the heaviest known element—uranium ($Z = 92$)—there are not sufficient extra-nuclear electrons left over to occupy all the possible O and P shells after the requirements of the K, L, M, and N shells have been satisfied.

The Inner Quantum Numbers of X-Ray Terms.—We have employed the Selection Principle $\Delta k = \pm 1$ for the purpose of determining the azimuthal quantum numbers of the X-ray terms, but an important restriction to its range of applicability has not yet been mentioned. With the azimuthal quantum numbers of the various X-ray terms allocated as above, the condition $\Delta k = \pm 1$ certainly holds for all observed combinations of terms, but the reciprocal proposition is not valid, that is to say, not all term combinations for which the azimuthal quantum number changes by unity occur as lines in the X-ray emission spectrum. In illustration of this we may take the actual combinations of L terms with M terms which are found in the L emission series of an element. For the L_{I} term $k = 1$, and this term should combine in emission only with M_{II} and M_{III}, for both of which $k = 2$. This is indeed the case, and both these lines are observed. On the other hand, for the L_{II} and L_{III} terms $k = 2$, and the combinations consistent with $\Delta k = \pm 1$ are now

$$(L_{\mathrm{II}} - M_{\mathrm{I}}),\ (L_{\mathrm{III}} - M_{\mathrm{I}}),\ (L_{\mathrm{II}} - M_{\mathrm{IV}}),$$
$$(L_{\mathrm{III}} - M_{\mathrm{IV}}),\ (L_{\mathrm{II}} - M_{\mathrm{V}}), \text{ and } (L_{\mathrm{III}} - M_{\mathrm{V}}).$$

Of these the first four and the last are observed, but not the combination $(L_{\mathrm{II}} - M_{\mathrm{V}})$. Examples of other term combinations which are permitted by the Selection Principle, but which are not actually observed are $(L_{\mathrm{II}} - N_{\mathrm{V}})$, $(M_{\mathrm{II}} - N_{\mathrm{V}})$, $(M_{\mathrm{IV}} - N_{\mathrm{VII}})$, and $(M_{\mathrm{V}} - N_{\mathrm{II}})$.

The failure of the Selection Principle to account for the absence of such lines as these must depend, of course, upon the fact that for each of the L, M, and N groups of internal electrons in the atom there are more energy levels, and therefore presumably more types of actual electronic orbits, than can be accounted for in terms of the n_k system of classification. The X-ray " term group " n_k certainly combines with any other term group n'_{k+1} or n'_{k-1}, but each of the two individual terms of the n_k group not necessarily with each individual term of the n'_{k+1} or n'_{k-1} group.

The apparently composite nature of each n_k energy level within the atom may formally be described by the use of a third quantum number j called the *inner quantum number* of the state in question. This parameter may provisionally be regarded as specifying a quantised condition of the radiating electron with respect to some further degree of freedom, either of itself or of the atom residue, which is not taken into account by the quantum numbers n and k. Each stationary state of each electron in the atom is then to be defined by the values of three quantum numbers n, k, and j. Until we know what the quantum number j actually refers to, it is, of course, impossible to be definite regarding its absolute value. Taking j as integral, however, a provisional enumeration of the inner quantum numbers of X-ray terms may be obtained as follows. For any given value of n, we know that there is only one X-ray term for which $k = 1$, but two terms for each value of k greater than 1. Accordingly, we assume that the possible values of j are k and $k - 1$, but that the value $j = 0$ is forbidden. Conventionally, the larger of any pair of terms of identical n and k is taken to correspond to the smaller value of j. The complete system of K, L, M, N, O, and P terms as found in the X-ray spectra of the heaviest of the elements is then depicted in terms of the corresponding values of n, k, and j as shown in Fig. 14. The horizontal lines represent the energy levels of the various sub-groups of internal electrons actually present in the extra-nuclear structure of the heaviest elements, the lowest energy level being that of the K group of electrons which is nearest the nucleus.

The lines actually observed in X-ray emission series are the term combinations represented by the vertical arrows connecting the different K, L, M . . . levels. The arrows finishing at the K level represent the lines of the K emission series, the arrows finishing at all three L levels represent the lines of the L emission series, etc. With our present enumeration of the subsidiary quantum numbers k and j, the Selection Principle for X-ray lines can now be modified to the form—

$$\Delta k = \pm 1, \Delta j = 0 \text{ or } \pm 1.$$

The only permitted transitions between the different internal energy levels are those for which the azimuthal quantum number changes by unity,

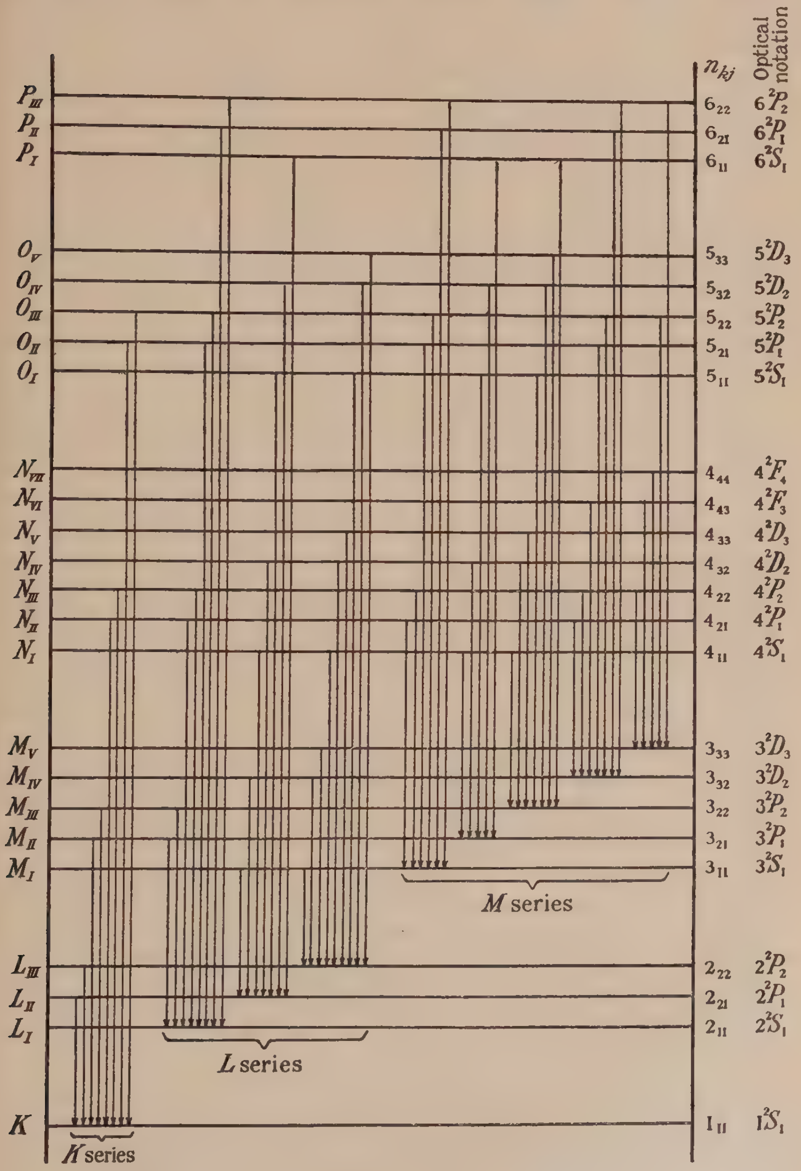
Optical notation
n_{kj}
P_{III} 6_{22} 6^2P_2
P_{II} 6_{21} 6^2P_1
P_I 6_{11} 6^2S_1
O_V 5_{33} 5^2D_3
O_{IV} 5_{32} 5^2D_2
O_{III} 5_{22} 5^2P_2
O_{II} 5_{21} 5^2P_1
O_I 5_{11} 5^2S_1
N_{VII} 4_{44} 4^2F_4
N_{VI} 4_{43} 4^2F_3
N_V 4_{33} 4^2D_3
N_{IV} 4_{32} 4^2D_2
N_{III} 4_{22} 4^2P_2
N_{II} 4_{21} 4^2P_1
N_I 4_{11} 4^2S_1
M_V 3_{33} 3^2D_3
M_{IV} 3_{32} 3^2D_2
M_{III} 3_{22} 3^2P_2
M_{II} 3_{21} 3^2P_1
M_I 3_{11} 3^2S_1
M series
L_{III} 2_{22} 2^2P_2
L_{II} 2_{21} 2^2P_1
L_I 2_{11} 2^2S_1
L series
K 1_{11} 1^2S_1
K series

FIG. 14.—Scheme of *X*-ray terms and emission lines.

while the inner quantum number simultaneously changes also by unity or remains unaltered. By examination of the k and j values given in the figure, it will be seen that this comprehensive Selection Rule takes account of the absence of the lines $(L_{\text{II}} - M_{\text{V}})$, $(L_{\text{II}} - N_{\text{V}})$, $(M_{\text{V}} - N_{\text{II}})$, etc., already mentioned.

We may now compare the fine structure of X-ray lines and terms with the composite structure of the lines and terms of optical series spectra. The major distinctions between the S, P, D, and F sequences of optical terms and the Selection Principle which governs their possible combinations to give spectral lines have already been referred to the different values of the azimuthal quantum numbers of the corresponding electronic orbits. However, the internal multiplicity of the terms of most optical series spectra and indeed the existence of separate and distinct systems of terms of different multiplicity for one and the same atom or ion receive no explanation in terms of two quantum numbers n and k only. The empirical facts regarding this multiplicity of optical terms have already been given in Chapter I., but we have purposely omitted reference to it in the theoretical correlation of optical terms with electron orbits earlier in the present Chapter. In Chapter I., each multiplet spectral term was provisionally identified by a sequence characteristic S, P, D, or F (which we now know to correspond to an azimuthal quantum number $k = 1, 2, 3$, or 4), by a serial number n (which is simply related to the principal quantum number n of the corresponding electronic orbit), and by an index r, equal to the multiplicity of the system to which the term belonged, thus: $\mathrm{n}^{r}D$. Further, a method of enumeration by suffices of the separate components of each multiplet term was outlined which, with the aid of a simple restricting rule, served to specify the actual combinations of the components of multiplet terms which are met with in optical emission spectra. This rule took the form that the suffix numerals of two combining terms can only differ by zero or by ± 1. The identity of this Selection Principle with that applying to the j's of the X-ray terms immediately suggests that the internal multiplicities of the optical and the X-ray terms must be referred to a common origin. The only real difference between X-ray terms and optical terms is that the former relate to energy states of the atom produced by the complete removal of one of its internal electrons, whereas the optical terms relate to energy states of the atom produced by displacement, but not complete removal, of one of the peripheral electrons. Both X-ray and optical terms are now found to be incompletely specified by the two quantum numbers n and k, and both require the inclusion of a third parameter—the inner quantum number—characteristic in some way of the sub-atomic state under consideration. The correspondence between the two multiplicities is further borne out by comparison of the X-ray system of terms with the doublet system of optical terms which comprise the arc spectrum of any one of the alkali metals or the spark spectrum of any of the alkaline earth metals. In the X-ray system there is for $k = 1$ a series of singlet terms analogous to the $^2S_1$ sequence of singlets; for $k = 2$, a series of doublet terms which is the counterpart of the $^2P_{1, 2}$ sequence of doublets, and so on. Further, the Selection Rules $\Delta k = \pm 1$ and $\Delta j = 0$ or ± 1 governing the combinations of terms are the same in both cases, so that the X-ray system of terms can properly be styled a doublet system of terms. With optical notation, the individual X-ray terms may, therefore, be symbolised as indicated on the extreme right of Fig. 14.

THE MEANING OF INNER QUANTUM NUMBERS.

We must now briefly discuss, from the standpoint of our mechanical model of the atom, the implications of the fact that each X-ray or optical spectral term requires at least three quantum parameters n, k, and j for its specification. We have up till the present considered that the interaction of any atom with radiation involves only the displacement of one electron—the radiating electron—between various stationary orbits, the remainder of the atom being thereby unaffected in shape and structure. The radiating electron itself has been regarded as a point charge, and the field of the atom residue as a central and spherically symmetrical field. Such a model permits of interpretation of the major characteristics of X-ray and optical terms through the medium of the two quantum numbers n and k which are involved in quantising the motion of the radiating electron in plane orbits (motion of two degrees of freedom), but it does not provide any further degree of freedom of the electron to which the inner quantum number j of the spectral terms can be referred. Provided the field is as described, all orientations of the electron's orbit to the atom residue are energetically equivalent.

The simplest way of interpreting j which suggests itself depends upon a denial of the above assumption that the atom residue presents such a central field to the radiating electron. It is indeed certain that in most actual cases the orbits of the electrons comprising the *atom residue* will be asymmetrically disposed about the main centre of force—the nucleus. On this account the atom residue must possess a definite resultant angular momentum about some preferential axis, and this being so the energy of the system (radiating electron + atom residue) with the electron moving in any particular orbit can no longer be regarded as independent of the orientation of this orbit with respect to the atom residue. Not all orientations, however, should be physically possible. Corresponding to the third degree of freedom of the electron which is made manifest by the asymmetry of the field in which it moves, a further quantum equation of restriction must be introduced which will effectively restrict to a few discrete values the angle which the plane of the orbit can make with the preferential axis of the atom residue. In effect, the total angular momentum of the atom, which is the vector sum of the angular momenta of the atom residue and of the radiating electron, is also quantised, and the hitherto unexplained inner quantum number j may be associated with this total angular momentum of the atom in terms of the relation

$$\text{total angular momentum} = \frac{jh}{2\pi},$$

analogous to the relation

$$\text{angular momentum of radiating electron} = \frac{kh}{2\pi}.$$

In place of a single spectral term for a given value of n and of k, there should then be a multiplet term with as many components as there are possible values of j consistent with the ascribed values of n and k. This interpretation of the inner quantum number is formally in agreement with the requirements of the Correspondence Principle, which is found to demand that the permitted changes of the total angular momentum of the atom $jh/2\pi$ should conform to the rule $\Delta j = 0$ or ± 1, already established empirically by analysis of the observed combinations of terms in both optical and X-ray spectra. Again, the occurrence of two or more distinct systems of terms of different multiplicities in the series spectrum of one and the same atom can be referred—at least formally—to the possibility of distinct and different values of the angular momentum of the atom residue.* When examined more closely, however, these concepts prove only partially successful in taking account of the actual multiplicities of the optical terms of the different elements and especially in explaining the fundamentally different effects of a magnetic field upon the individual components of each multiplet term (cf. p. 29). It lies outside our province to attempt to discuss the many anomalies met with in attempting to fit the concepts to all the experimental facts of term multiplicities and of the Zeeman resolution of spectral lines. One single illustration will suffice to indicate their inadequacy. We have every reason to believe that the neutral atom of each alkali metal comprises a single valency electron and an atom residue of a specially stable and symmetrical type—the structure characteristic of the preceding inert gas atom. This type of atom residue above all others is unlikely to possess any resultant angular momentum about a preferential axis, and accordingly all orientations of an n_k orbit of the valency electron in the alkali metal atom should be equivalent energetically, that is, the arc spectral terms should all be singlets. Actually, however, the system of optical terms in the arc spectrum of any one of the alkali metals is a doublet system, that is, there are two possible values of j for each value of k (excluding $k = 1$). In this case, either we must assume that the inert gas-like residue is asymmetrical, in the face of all physical and chemical evidence, or we must suppose that the radiating (valency) electron itself possesses the additional degree of freedom which is required to account for the term multiplicity.

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* It may be noted that here we are departing from the simple premise that the atom residue remains unaltered in quantum jumps of the radiating electron. We are in effect assuming that its angular momentum remains the same for all quantum jumps of this electron between orbits corresponding to terms of the same system, but alters during any quantum jump between orbits corresponding to terms of different systems (different multiplicities).

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The Spinning Electron.—The solution of the difficulty presented by the doublet character of the spectra of the alkali metals has been obtained within recent years through the introduction by Goudsmit and Uhlenbeck of the concept of *the spinning electron*. According to this theory the electron itself is no longer treated as a point particle but is assumed to possess an internal axis of spin and an intrinsic angular momentum of spin of half a Bohr unit, viz. $\frac{1}{2}(h/2\pi)$. This gives to the electron an invariant spin quantum number $s = \frac{1}{2}$ and, in addition, a further degree of freedom of orientation with respect to its orbit in the atom. In such atoms or ions as possess only one electron in the valency shell, the atom residue having no resultant angular momentum, the total angular momentum $jh/2\pi$ of the atom or ion in any stationary state is now obtained by compounding the intrinsic angular momentum $\frac{1}{2}(h/2\pi)$ of the electron itself with a vector $lh/2\pi$ which corresponds to the angular momentum of the electronic orbit. This new quantum number l—*the serial quantum number* *—takes the place of the azimuthal quantum number k of the old theory, and is numerically equal to $k - 1$. Thus $l = 0, 1, 2, 3 \ldots$ for $S, P, D, F \ldots$ terms respectively.

By the vector compounding, the values of j are limited by the condition:—

$$|l - s| \leqq j \leqq |l + s|,$$

and, since $s = \frac{1}{2}$, the only "quantised" values of j which are possible for the alkali metal atom are thus $l + \frac{1}{2}$ and $l - \frac{1}{2}$. Hence, for the $S, P, D, F \ldots$ terms of the doublet system, j has the following values:

$$\begin{aligned} &S(l = 0), \quad j = \tfrac{1}{2}\,{}^{**} \\ &P(l = 1), \quad j = \tfrac{1}{2} \text{ or } \tfrac{3}{2} \\ &D(l = 2), \quad j = \tfrac{3}{2} \text{ or } \tfrac{5}{2} \\ &F(l = 3), \quad j = \tfrac{5}{2} \text{ or } \tfrac{7}{2} \end{aligned}$$

It will be seen that the values of j obtained in this way are each half a unit less than the integral suffices previously used in the empirical designation of the doublet components. The 1^2S_1 term of the alkali metal spectrum should more correctly be written $1^2S_{\frac{1}{2}}$, the $2^2P_{1,2}$ doublet $2^2P_{\frac{1}{2},\frac{3}{2}}$, and so on. It is, however, convenient to retain the use of the integral suffices, remembering that the true inner quantum number of any component of a doublet term is numerically less than the suffix used by half a unit. The Selection Principle $\Delta j = 0$ or ± 1 holds equally well, of course, when all values of j are increased by the same amount.

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* The exact significance of l is made clear in the Schrödinger Wave Mechanics.

** The $j = -\frac{1}{2}$ state is indistinguishable physically from the $j = \frac{1}{2}$ state.

The *spark* spectrum of any element of Group II of the Periodic Classification derives also from a doublet system of terms of essentially the same type as that which characterises the arc spectrum of the alkali metal atom. The similarity between the two types of spectra is not surprising, since the singly ionised atom of calcium or strontium or barium bears a distinct structural resemblance to the neutral alkali metal atom, both consisting of a single valency electron and a highly symmetrical, inert gas-like, atom residue, which presumably remains undisturbed by quantum jumps of the valency electron. Assuming that this atom residue has no resultant angular momentum, each optical energy level of the atom or ion is then characterised solely by the quantum parameters n, k, j or n, l, j of the orbit of the single outer electron.

New Interpretation of Optical Terms.—Turning now to the *arc* spectra of the elements of Group II, we are confronted with the fact that there are two distinct systems of optical terms—a singlet and a triplet system—in each spectrum. An empirical enumeration of the inner quantum numbers of these terms which is consistent with the Selection Rule $\Delta j = 0$ or ± 1 has already been given in Chapter I. The singlet system is represented by $({}^1S_0, {}^1P_1, {}^1D_2, {}^1F_3)$, the triplet system by $({}^3S_1, {}^3P_{0,1,2}, {}^3D_{1,2,3}, {}^3F_{2,3,4})$. In order to explain the occurrence of two systems of optical terms in the same spectrum, it now becomes necessary to abandon the assumption hitherto followed that each optical term or energy level of the atom can be described uniquely in terms of the quantum parameters of a single "radiating electron." This only holds good when there is but one electron present in the valency shell of the atom or ion considered. When there are two or more electrons in this shell, these "react" upon one another in a certain sense, and the complete description of any energy level of the atom as a whole then depends upon the exact quantum state of every electron in the valency shell.

Each single electron in this valency shell may be designated by three quantum numbers n, l, and s. The principal quantum number n determines to a first approximation the energy level of the electron, the serial quantum number l determines its orbital angular momentum, and the spin quantum number $s(= \frac{1}{2})$ determines its angular momentum of spin. Both l and s are to be treated as vectors contributing towards the total angular momentum of the atom. The state of the atom as a whole is defined by (a) the principal quantum numbers n of all its peripheral electrons, (b) a group quantum number L which is the vector resultant of the individual l's of these electrons, and (c) a spin quantum number S which is the vector resultant of the individual s's of these electrons. Here again the vectors L and S compound to give the inner quantum number j, which therefore represents the total number of units of angular momentum which the atom possesses in the state in question. The angular momentum of the atom residue inside the valency shell is itself taken to be zero.

It is the group quantum number L and not the l of any single electron which determines the type of the spectral term corresponding to the state of excitation of the atom under consideration. For $L = 0$ we have an *S* term, for $L = 1$ a *P* term, etc. Again, since each s is equal to $\frac{1}{2}$, S itself is either integral or half-integral. The actual value of S determines the multiplicity r of the system to which the term belongs, r being given by the relation

$$r = 2S + 1.$$

Thus for $S = 0$, $r = 1$ (singlet system); for $S = \frac{1}{2}$, $r = 2$ (doublet system); for $S = 1$, $r = 3$ (triplet system); etc. The possible values of j for the *S*, *P*, *D*, *F* . . . terms of different systems, obtained by compounding the vectors L and S, are then given by the condition

$$|L - S| \leqq j \leqq |L + S|,$$

and are as shown in Table V.

TABLE V.

Possible Values of the Inner Quantum Number j in Different Systems.

Term.	L.	Singlet System ($r = 1$, $S = 0$).	Doublet System ($r = 2$, $S = \frac{1}{2}$).	Triplet System ($r = 3$, $S = 1$).
S	0	0	$\frac{1}{2}$	1
P	1	1	$\frac{1}{2}$ $\frac{3}{2}$	0 1 2
D	2	2	$\frac{3}{2}$ $\frac{5}{2}$	1 2 3
F	3	3	$\frac{5}{2}$ $\frac{7}{2}$	2 3 4

Term.	L.	Quartet System ($r = 4$, $S = \frac{3}{2}$).	Quintet System ($r = 5$, $S = 2$).	Sextet System ($r = 6$, $S = \frac{5}{2}$).
S	0	$\frac{3}{2}$	2	$\frac{5}{2}$
P	1	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$	1 2 3	$\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$
D	2	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$	0 1 2 3 4	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$
F	3	$\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$	1 2 3 4 5	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$ $\frac{11}{2}$

Term.	L.	Septet System ($r = 7$. $S = 3$).	Octet System ($r = 8$, $S = \frac{7}{2}$).
S	0	3	$\frac{7}{2}$
P	1	2 3 4	$\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$
D	2	1 2 3 4 5	$\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$ $\frac{11}{2}$
F	3	0 1 2 3 4 5 6	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$ $\frac{11}{2}$ $\frac{13}{2}$

These are in accord with the values which must formally be ascribed to the j's of spectral terms to make their observed combinations comply with the Selection Rule $\Delta j = 0$ or ± 1. The only difference between this theoretical system of enumeration of the j's and that in common usage is that in practice the j's of terms belonging to systems of even multiplicity are for convenience made integral by the addition of half a unit to each.

It will be sufficient to illustrate the new method of interpretation of spectral terms by reference to the singlet and triplet systems in the arc spectrum of any element of Group II. Each of these elements possesses two valency electrons and an atom residue of the inert gas type which has no intrinsic angular momentum. The total angular momentum of the atom therefore depends upon the orbital angular momenta and the spin angular momenta of the two valency electrons. For each atom the normal state is found to be represented by a ${}^1S_0$ term. The fact that this is an S term means that in the normal state the two valency electrons have a combined orbital angular momentum of zero ($\mathrm{L} = 0$); the fact that the term belongs to a singlet system means that the two electrons have a combined angular momentum of spin of zero ($\mathrm{S} = 0$). We therefore conclude that in the normal state both electrons occupy equivalent $l = 0$ (or $k = 1$) orbits and that their directions of spin are opposed to one another.

Most of the optical states of excitation of the atom can now be interpreted by supposing that one of the two valency electrons always remains in its normal orbit, while the other valency electron occupies various orbits of greater energy content. For example, the two valency electrons of the normal magnesium atom both occupy 3_1 orbits (n_k designation). The electronic configuration of the valency shell in various other states of excitation of the atom and the spectral terms corresponding are shown in the following scheme :—

Electronic Configuration.	*Spectral Term.*	
$2(3_1)$	${}^1S$	normal.
$1(3_1),\ 1(n_1)$	${}^1S$ or ${}^3S$	
$1(3_1),\ 1(n_2)$	${}^1P$ or ${}^3P$	
$1(3_1),\ 1(n_3)$	${}^1D$ or ${}^3D$	
$1(3_1),\ 1(n_4)$	${}^1F$ or ${}^3F$	
$2(3_2)$	${}^1S'$, ${}^1D'$, ${}^3P'$	anomalous.
$1(3_2),\ 1(3_3)$	${}^1P'$, ${}^1D'$, ${}^1F'$, ${}^3P'$, ${}^3D'$, ${}^3F'$	

The l of one of the electrons being zero in every case, it happens that the l of the displaced electron ($= k - 1$) is identical with the resultant L of both, so that the S, P, D, F terms have the same meaning as regards the nature of the orbit of the displaced electron as when there is a single valency electron, viz. an S term means an n_1 orbit, a P term an n_2 orbit, etc. The difference between singlet and triplet terms of the same type lies in their different values for S. For all singlet terms $\mathrm{S} = 0$, that is, the angular momenta of spin of the two valency electrons cancel one another, and the total angular momentum j of the atom is then simply equal to the compounded orbital angular momenta L of the two electrons. For all triplet terms $\mathrm{S} = 1$, that is, the spins of the two valency electrons reinforce one another, and j has then as many values as can be obtained by compounding the vectors L and S, namely, $|\mathrm{L} - \mathrm{S}|$, $|\mathrm{L}|$, and $|\mathrm{L} + \mathrm{S}|$.

Anomalous Terms.—While the majority of the lines in the arc spectra of the elements of Group II are represented by combinations of the above types of terms, there are also quite a number of lines involving terms which, although they possess the superficial characteristics of *S*, *P*, *D*, and *F* singlet and triplet terms, nevertheless cannot be fitted into the normal singlet and triplet systems. These "anomalous terms" are distinguished from the normal terms by being written $^1S'$, $^1P'$, $^3P'$, etc. Their most interesting and significant feature is that several of them are *negative* in value. This means that the atom can assume optical states of excitation of greater energy than would correspond to the complete removal of the "radiating electron" (the electron involved in the normal spectral terms) from its most stable position in the atom to infinity. Accordingly, we must conclude that the anomalous terms correspond either to the displacement in the atom of another electron more tightly bound than the normal "radiating electron," or to *the simultaneous displacement of both the valency electrons from their normal to outer orbits.* A detailed examination of the nature of anomalous terms has shown that the latter interpretation is the correct one. Here, it will be noted, we finally lose contact with the mechanical picture of the atom as comprising a positive residue and a single radiating electron, which has been of such immense service in the theoretical development of the quantum theory of line spectra.

For magnesium, anomalous spectral terms are found which correspond to (1) both valency electrons in 3_2 orbits, (2) one valency electron in a 3_2 orbit, the other in a 3_3 orbit. These are indicated in the lower part of the above table. It will be seen that quite different types of anomalous terms may correspond to one and the same n_k configuration of the valency shell. The actual type of the spectral term is no longer determined by the k or l of one electron but by the resultant L of the two electrons. With both electrons in 3_2 orbits, $l_1 = 1$ and $l_2 = 1$, and the possible values of L are 0, 1, and 2 (S', P', and D' terms). With one electron in a 3_2 orbit and the other in a 3_3 orbit, $l_1 = 1$, $l_2 = 2$, and the possible values of L are now 1, 2, and 3 (P', D', and F'). The multiplicity of the system to which the term belongs is as before determined by the resultant angular momentum of spin S of the two electrons.

The observed combinations in emission of anomalous spectral terms with one another and with normal terms indicate that spontaneous changes which only involve the transfer of one of the displaced electrons to an inner orbit are still subject to the restriction Δk or $\Delta l = \pm 1$ for this electron. A few examples of such spontaneous transitions are found in the arc spectrum of magnesium in the observed combinations of the $^1S'$, $^1D'$, and $^3P'$ terms with the ^1P and ^3P terms, and of the $^1P'$, $^1D'$, etc. terms with $^1S'$, $^1D'$, $^3P'$, and ^1D terms. The $^1S'$, etc. terms do not, however, combine in emission with the ^1D, the ^3D, or the ^1S terms. Such combinations, which would involve the simultaneous transition of two electrons, the k or l of each electron altering by one unit, are forbidden. This is not to say that the simultaneous transition of two electrons with the emission of monochromatic radiation never occurs. Such spontaneous processes are, in fact, a common feature of most complex spectra which involve anomalous terms, but the only permitted transitions are such that, while the k or l of the one electron changes by one unit, that of the other electron simultaneously changes by two units, viz. $\Delta k_1 = \pm 1$, $\Delta k_2 = \pm 2$.

New Meaning of X-Ray Terms.—One or two points remain to be cleared up before we leave this Section. In the first place we must enquire how the above interpretation of the quantum characteristics of optical terms applies to the X-ray terms. Here we shall find it necessary to revise our views regarding the exact nature of X-ray terms, and we shall further find that our previous sub-division of the main K, L, M, N . . . groups of internal electrons in the atom into $n_{k,j}$ sub-groups is to some extent illusory. There are certainly three different L, five different M, and seven different N X-ray terms, but it is not correct to conclude from this that in the completed L, M, N . . . shells of electrons there are corresponding multiplicities of types of electronic orbits. Actually the orbits of the electrons in each main group are only to be distinguished by their values of l or k, so that in the K, L, M, N . . . shells we have the following types of electronic orbits :—

	K	L		M			N			
n_k	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4
$l(=k-1)$	0	0	1	0	1	2	0	1	2	3

Each n_k sub-group of internal electrons when completely developed in the atom must possess a very marked symmetry of disposition of the orbits in space, a symmetry which must be taken to imply that the sub-group vectors L, S, and j are all equal to zero. The sub-group becomes asymmetric and acquires values of S and j different from zero when an electron is removed from it.

Now each X-ray term denotes the energy required to remove an electron from a completed inner sub-group. We have previously worked on the basis that the X-ray term should be described in terms of the quantum characteristics of the normal orbit of this electron. The energy required to remove the electron must, however, depend not only upon the nature of the sub-group from which it comes but also upon the condition in which the depleted sub-group is left. It therefore appears that the nature of the X-ray term should more properly be characteristic of this incompletely developed sub-group of electrons which remains. On this basis, the necessity for the use of three quantum numbers in the specification of an X-ray term becomes readily intelligible. The quantum numbers required are obviously (a) the common principal quantum number n of all the electrons in the sub-group, (b) the group quantum number L of the incomplete group, and (c) the inner quantum number j of the incomplete group. Taking first of all the K (1_1) group of electrons, when one electron is removed from this group there is only one possible condition of the depleted shell. Before the removal of the electron, $\mathrm{L} = 0$, $\mathrm{S} = 0$, and $j = 0$; after its removal, $\mathrm{L} = 0$, $\mathrm{S} = \frac{1}{2}$, and $j = \frac{1}{2}$. Hence the single *K* term is characterised by ($n = 1$, $\mathrm{L} = 0$, $j = \frac{1}{2}$). Similarly, when an electron is removed from *any* n_1 sub-group, the sub-group suffers no change in L, since the l of each electron is zero, but S alters by $\frac{1}{2}$, hence j also alters by $\frac{1}{2}$. Hence the *X*-ray term corresponding to the removal of an electron from any n_1 sub-group is characterised by ($n = n$, $\mathrm{L} = 0$, $j = \frac{1}{2}$), and is single valued. For the 2_1, 3_1, 4_1 . . . sub-groups, these single valued *X*-ray terms are those previously designated as L_{I}, M_{I}, N_{I} . . . On the other hand, when an electron is removed from the n_2 type of sub-group, the sub-group thereby loses a unit of orbital angular momentum and half a unit of angular momentum of spin, so that for the incomplete sub-group $\mathrm{L} = 1$ and $\mathrm{S} = \frac{1}{2}$. There are now two possible values of j, namely $\frac{1}{2}$ and $\frac{3}{2}$, and the *X*-ray term is therefore a doublet ($n = n$, $\mathrm{L} = 1$, $j = \frac{1}{2}, \frac{3}{2}$). For the different sub-groups 2_2, 3_2, 4_2 . . . the doublet *X*-ray terms concerned are the components (L_{II}, L_{III}), (M_{II}, M_{III}), (N_{II}, N_{III}), etc. Similarly, the *X*-ray terms corresponding to the removal of electrons from the various n_3 sub-groups are also doublets characterised by ($n = n$, $\mathrm{L} = 2$, $j = \frac{3}{2}, \frac{5}{2}$), and these are to be identified with the doublets (M_{IV}, M_{V}), (N_{IV}, N_{V}), etc. in the *X*-ray system of terms. When we compare the new quantum parameters of the *X*-ray terms with those previously used (cf. Fig. 14), we see that, in effect, the old azimuthal quantum number k is to be replaced by the sub-group quantum number L which is always one unit less than k, and the empirical inner quantum number j is to be replaced by the true inner quantum number which is always half a unit less than the old value. It may be noted that in the new designation the very close analogy between the *X*-ray term system and an optical doublet term system is still preserved.

The Spectral Terms of Hydrogen.—The quantitative interpretation by Sommerfeld of the fine structure of the hydrogen arc lines furnished the first justification for the use of the n_k system of classification of electronic orbits. It may reasonably be asked how the hydrogen atom is to be dealt with in terms of a spinning electron and a serial quantum number l in place of the azimuthal quantum number k. The new model of the hydrogen atom must, of course, be very similar to the model which we have used to represent the neutral alkali metal atom, the only difference being that the single valency electron of hydrogen moves in a strictly Coulomb field, whereas in the alkali metal atom the field though still central is non-Coulomb. The possible energy levels of the hydrogen atom must then be characterised by the quantum numbers n, l, and j of the electron's orbit, and the system of spectral terms must be a doublet system of essentially the same nature as that of an alkali metal atom. Accordingly, for $n = 1$ there should be a single spectral term 1^2S_1, for $n = 2$ three spectral terms 2^2S_1, 2^2P_1, and 2^2P_2, for $n = 3$ five spectral terms 3^2S_1, 3^2P_1, 3^2P_2, 3^2D_2, and 3^2D_3, etc. Actually, however, a detailed examination of the fine structure of the hydrogen lines shows that, while there is a single $n = 1$ term, there are only two energetically different $n = 2$ terms and three $n = 3$ terms. The apparent discrepancy may be related to the fact that in the case of hydrogen as distinct from any alkali metal the electron moves in a strictly Coulomb field of force. The discrepancy vanishes if we assume that for the motion of an electron in such a field, orbits with the same principal quantum number n and the same inner quantum number j are energetically equivalent. This makes for hydrogen the 2^2S_1 term equal to the 2^2P_1, the 3^2S_1 term equal to the 3^2P_1, and the 3^2P_2 term equal to the 3^2D_2, so that effectively there are only two distinguishable $n = 2$ terms and three distinguishable $n = 3$ terms. Some theoretical justification for the above assumption has been obtained on the basis of the new quantum mechanics of Heisenberg.

GROUPING OF ELECTRONS IN THE ATOM. THE PERIODIC CLASSIFICATION.

In discussing certain of the optical properties of atoms we have not yet had to enquire too closely into the details of their internal structures. We may now indicate how the results of the quantum interpretation of optical and X-ray spectra may be combined with a knowledge of the other physical and chemical properties of the atoms to construct models which will express in each case the detailed grouping of all the extra-nuclear electrons around the nucleus.

For almost any atom we can infer from its chemical properties how many of its electrons occupy orbits which constitute the peripheral or valency shell. Further, the optical spectrum of the element often permits us to deduce the major characteristics of the orbit actually occupied by one of these valency electrons in the normal atom. In particular we have seen how the principal and azimuthal quantum numbers * of the orbit of the radiating electron of an atom in its most stable configuration may be deduced from the nature of the largest optical term in its arc spectrum. Regarding the other peripheral electrons in atoms of valency greater than one, the arc spectrum does not afford much direct information, but, with Bohr's Postulate of the Invariance of Quantum Numbers, the characteristics of the normal orbits of these electrons also are obtainable in many cases from a study of the spectra of higher order of the element. The Postulate referred to forms the basis of Bohr's method of atom-building, whereby the neutral atom of atomic number Z is considered to be synthesised from the stripped nucleus of $+^{ve}$ charge Ze by progressive capture and binding of electrons one by one to it. At each stage in the building up of the atom in this way the electron last added finally occupies that quantised orbit which is most stable with respect to the nucleus and the electrons already bound. The important

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* Throughout the present Section we use the older method of designation of electronic orbits.

assumption is now made that, while the addition of each electron to the system naturally affects the strength of binding of all the other electrons which have gone before and therefore the dimensions of the system, it nevertheless leaves unchanged the quantum numbers which characterise the orbits of these electrons. Accordingly, if the quantum numbers for the orbit occupied by the last added electron at any stage in the synthesis of the atom are known, it is to be assumed that the orbit of this electron in the normal neutral atom is defined by these same quantum numbers. The stages in the capture and binding of the last electron to the singly ionised atom residue to form the neutral atom are manifest optically in the lines of the arc spectrum of the element, and, as already mentioned, an analysis of the terms of this spectrum serves to fix the quantum parameters of the most stable orbit occupied by this electron. On the other hand, the spark spectrum of the first order of an element represents the various stages in the capture and binding of the electron last but one in the formation of the neutral atom, the spark spectrum of the second order represents the various stages in the capture and binding of the electron last but two, and so on. Accordingly, by analysis of the terms of the spark spectra of various orders of an element, a method is afforded of determining the quantum numbers of the orbits of the radiating electron in the singly ionised atom, in the doubly ionised atom, etc., and by hypothesis these quantum numbers remain characteristic of the orbits of these same electrons in the neutral atom also. We may consider the case of the magnesium atom in illustration of this principle. First of all, however, we must introduce a more convenient system of nomenclature which will serve to distinguish the spectra of different order of any element. The arc spectrum of an element M, which is the spectrum of the neutral atom M, we refer to simply as the spectrum of M(I); the spark or enhanced spectrum of the first order, which is really the spectrum of the singly ionised unit M^+, we refer to as the spectrum of M(II), etc. Now the term analysis of the spectrum of Mg(I) shows (cf. Table IV.) that the principal and azimuthal quantum numbers of the largest term are 3 and 1 respectively. The normal orbit of the last captured electron to form the neutral magnesium atom is therefore taken to be a 3_1 orbit. Again the largest term in the spectrum of Mg(II) also corresponds to $n = 3$, $k = 1$, so that the normal orbit of the last captured electron to form singly ionised magnesium Mg^+ is again a 3_1 orbit. It follows then that in the neutral magnesium atom, both the valency electrons which form the peripheral shell of the atom occupy 3_1 orbits. A similar term analysis of the spectra of Al(I), Al(II), and Al(III) shows that the largest term in the first corresponds to $n = 3$, $k = 2$, while the largest terms in the second and third both correspond to $n = 3$, $k = 1$. From this we conclude that the three valency electrons constituting the outer shell in the neutral aluminium atom are arranged, two in 3_1 orbits and the third—the most loosely bound since it is the radiating electron in the arc spectrum of the element—in a 3_2 orbit. From these examples, it will be evident that by a systematic examination of the data of optical series spectra, a great deal of information can be obtained regarding the orbits of the outermost or valency electrons of many of the elements.

Turning now to a consideration of the electrons inside the peripheral shell, we have seen from an examination of the X-ray spectra of the elements that the electrons within the heavier atoms are distributed between a number of main energy levels denoted by K, L, M, N . . ., and we have found that the orbits of electrons occupying these different energy levels are primarily characterised by principal quantum numbers 1, 2, 3, 4 . . . respectively. We have regarded these inner electrons as grouped into rings or shells around the nucleus, the successive rings or shells counting from the nucleus outwards corresponding to a progressively increasing principal quantum number. Further, it has been found that, whereas there is a single K energy level within any atom, the L, M, N . . . energy levels are multiple, a result which is explicable on the assumption that each main shell of inner electrons is divided into energetically distinct sub-groups which correspond to the same principal quantum number but different values of the azimuthal quantum numbers of the electronic orbits concerned.

Since the number of internal sub-groups obtained in this way is very limited even for the heaviest elements, it is obvious that in general several electrons must occupy identical energy levels within the atom, and the problem then presented is how many electrons belong to each internal energy level in the various atoms. In approaching this problem, however, a preliminary question which demands attention is whether the several internal electrons which occupy one and the same energy level move in equivalent but spatially distinct orbits or whether they share a common ring orbit about the nucleus. In the earlier days of the quantum theory of atomic structure when only circular orbits were recognised for the single electron of the hydrogen atom, the second alternative was employed to construct plane models of the other atoms with the extra-nuclear electrons arranged in a few concentric rings about the nucleus, each ring carrying several electrons. With the recognition of elliptic as well as circular orbits for the electrons, attempts were still made to evolve working "ring" models with the electrons in each ring traversing congruent elliptical paths. Quite apart from the dynamical instability inherent in all such models, however, they fail to take account of the spatial structures of the real atoms, and they fail also when subjected to quantitative test to explain many of the properties of the X-ray spectra of the atoms. We are thrown back then upon the first assumption, which is indeed now fundamental to modern atomic theory, that while the electrons in one and the same sub-group move in orbits which are exactly equivalent in shape and size, these orbits are nevertheless spatially separate and distinct from one another. The orbits described by the electrons of any sub-group within the atom must, of course, be regarded as exhibiting spatial symmetry. Into the details of this, however, or indeed into any quantitative dynamical analysis of the present-day atom models, it is as yet impossible to enter. The virtue of these models lies in the fact that, however complex they may be dynamically, they give a very convincing qualitative picture of the various physical and chemical properties of the atoms. We do not propose to give a full account of all the evidence, chemical and physical, which serves to decide the number of electrons comprising the different groups or shells in the various atoms. The main facts may be briefly summarised as follows.

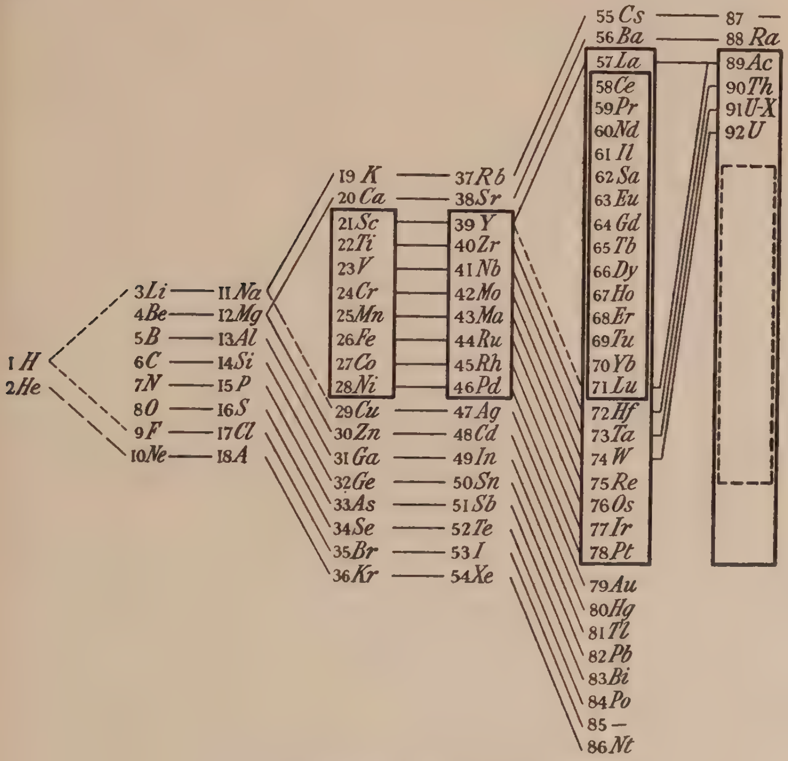

FIG. 15.—The Periodic System of the elements.

When the elements are arranged in order of their atomic numbers and in periods which represent the periodicity in their chemical properties as in Fig. 15—a presentation of the Periodic Classification originally due to J. Thomsen,—it is seen that each period of elements ends with an inert gas. The atoms of these particular elements are characterised by a peculiar chemical and physical stability. They form no stable compounds in themselves or with any of the other elements, and further they are ionised, that is, an electron is abstracted from their outer shell of electrons, only with great difficulty. We therefore regard the outer shell of electrons in any of the inert gases as possessing a peculiarly stable configuration which must involve a high degree of spatial symmetry in the disposition of the orbits of the outer electrons. This view is supported by the properties of the atoms which immediately precede and succeed the inert gases in the table. The halogens are strongly electronegative in character, in that the halogen atom in its chemical reactions readily acquires an additional electron with formation of the negatively charged halogen ion. On the other hand, the alkali metals are all strongly electropositive, that is, the electron last added to form the neutral alkali metal atom is easily removed, giving the positively charged ion. These facts point to the conclusion that the outer shell of electrons in the neutral halogen atom lacks but one electron to give it the stable configuration characteristic of the outer shell of electrons in the inert gas atom which follows it, whereas the valency electron of the neutral alkali metal atom is a loosely attached electron revolving outside the same stable shell of the inert gas type. The electronegative and electropositive characters of halogen and alkali metal respectively are due to the endeavour of the atom of halogen or alkali metal to gain or lose an electron and so acquire this outer stable configuration. The stability of the outer shell of electrons in each inert gas gives this group of elements a special significance in relation to the process of building up the electronic atmospheres of the elements. A clue to the nature of the stable configuration of outer electrons of each inert gas is afforded by the arc spectrum of the alkali metal which succeeds it in the Periodic Classification. From Table IV. (p. 82) we see that the valency electron of lithium normally occupies a 2_1 orbit, that of sodium a 3_1 orbit, that of potassium a 4_1 orbit, and so on. The obvious presumption then is that, in the inert gas at the end of each period, the outer shell consists of electrons occupying orbits of total quantum number one unit less than that of the valency electron of the alkali metal which follows. Hence we infer that in the building up of the atoms in order of their atomic numbers, the successive periods of Fig. 15 are primarily concerned in the development of outer shells of electrons in orbits of progressively increasing total quantum number. In the first period H—He the one-quantum shell is initiated, in the second period Li—Ne the two-quantum outer shell is initiated, etc.

This scheme of the gradual development of shells with increasing atomic number is supported by the fact that in the X-ray spectra of the elements the K internal energy level, which corresponds to an $n = 1$ group of electrons as an *internal* shell, is first encountered in the elements of the second period, the L internal energy levels ($n = 2$) in the elements of the third period, etc.

The numbers of elements in the different periods of the Periodic Classification are given by 2, 8, 8, 18, 18, 32, and from what has been said it might be imagined that these should represent the numbers of electrons in the completely developed K, L, M, N, O, and P shells respectively within the heaviest atoms. This, however, is not the case. The L, M, N, O, and P energy levels are multiple, and we must distinguish clearly between the complete development of any main quantum group of electrons within the atom and the complete development of any one of the sub-groups which comprise it. From our interpretation of these sub-groups in terms of the azimuthal quantum numbers of the electronic orbits concerned, it follows that the completely developed n-quantum group should contain altogether n sub-groups with $k = 1$, $k = 2$, $k = 3$, . . . $k = n$. Now for each n_k sub-group for which $k > 1$ there are two X-ray terms, hence the total number of X-ray terms corresponding to a completely developed n-quantum group must be $(2n - 1)$. This may now be used as a criterion to decide whether in any atom any particular shell of internal electrons is completely developed. For the heaviest known elements, radium, thorium, etc., the actual numbers of K, L, M . . . terms found in their X-ray spectra are as follows: one K, three L, five M, seven N, *five* O, and *three* P terms. While then it is probable that in the internal structure of these atoms the one, two, three, and four-quantum groups of electronic orbits are completely developed, it is clear that the five and six-quantum groups are only partially developed. This must mean that in the gradual building up of these atoms from the stripped nucleus by progressive addition of electrons, a stage is reached in filling up the O shell of electrons and before this shell is completed, when the next added electrons find their most stable positions in certain P (six-quantum) orbits instead of in any of the five-quantum orbits which remain to be filled. Again, from the X-ray spectra of the atoms Cs, Ba, etc. immediately following xenon, it is found that there are one K, three L, five M, *five* N, and *three* O X-ray terms, hence in these atoms the one, two, and three-quantum groups are probably completely developed, but not the four and five-quantum groups. Comparing this stage of development with that in the atoms Ra, Ac, etc. at the beginning of the next period, it follows that in the construction of the atoms in the long period of elements between xenon and niton, the thirty-two electrons which represent the difference in the electron atmospheres of these two inert gases must be used not only for the gradual development of the P shell which is the outer shell of electrons in niton, but also for completing the development of the four-quantum (N) group of electronic orbits and for carrying to a further stage the development of the five-quantum (O) group. Similarly, in passing from krypton which has one K, three L, five M, and three N X-ray terms to xenon, the eighteen added electrons are used not only to form the outer O shell in xenon but also to carry on the development of the four-quantum N shell; also in passing from argon to krypton the eighteen added electrons go partly to form the outer N shell of electrons in krypton, partly to complete the development of the internal M shell of electrons. This concept, which is suggested by the *X*-ray spectra of the elements, of the filling up of the incompletely developed internal shells of electrons within each of the long periods of elements in the Periodic System is of very great significance in the present theory of atomic structure, by virtue of the explanation which it offers of the anomalous properties of the so-called transition elements and the rare earth metals which occur (bracketed) in the fourth, fifth, and sixth periods of Fig. 15.

Reverting again to the question of the numbers of electrons which actually occupy the various shells (complete or incomplete) in the different chemical atoms, we may now enquire what is the maximum number of electrons which will represent the complete development of any particular group or sub-group of orbits. Bohr originally considered that the maximum number of electrons which could belong to the same n_k sub-group in the atom should be $2n$, from which it follows that the maximum number of electrons in each completed n-quantum group should be $2n^2$. This latter result is still held to be true, but Bohr's original scheme for the distribution of the internal electrons in the n_k sub-groups has been considerably modified within recent years, chiefly as a result of detailed analysis of the chemical and the physical properties of the elements by Main Smith and Stoner respectively. In the new scheme, the number of electrons in each fully-developed n_k sub-group is taken to be equal to $2(2k - 1)$. The number of electrons in a fully-developed n-quantum group is then given by

$$\sum_{k=1}^{k=n} 2(2k - 1) = 2n^2,$$

identical with the result of Bohr's original scheme. It may be mentioned that the Main Smith-Stoner distribution of electrons in the n_k sub-groups acquires a certain measure of theoretical justification in terms of the recent concept of the spinning electron and the ultimate significance of the inner quantum numbers of the *X*-ray and optical terms.

We may now give without further discussion the scheme which is finally obtained for the distribution of the electrons in the atoms of the rare gases. Table VI. gives the distribution of the electrons as regards the main n-quantum groups or shells; Table VII. shows the details of the development of the n_k sub-groups.

It will be seen that in the building up of the electron atmospheres of the atoms, the first and second quantum groups are regarded as completely developed at the end of the first and second periods respectively. In passing from neon to argon, the eight further electrons which are added take up three-quantum orbits, but these do not complete the three-quantum group. This group is only fully developed in the next (the first long) period where at the same time the four-quantum outer shell of krypton is begun. Again, in passing from krypton to xenon the development of this four-quantum group is carried to a further stage (but not completed) and simultaneously the five-quantum valency shell of xenon is formed. Only in the next and longest period, xenon to niton, is the development of the four-quantum group carried to completion, while here also that of the five-quantum group is continued and the six-quantum valency shell of niton is formed. It will be noted that the scheme embodies the

TABLE VI.

Shell $n =$	K 1	L 2	M 3	N 4	O 5	P 6
Helium . .	2					
Neon . .	2	8				
Argon . .	2	8	8			
Krypton . .	2	8	18	8		
Xenon . .	2	8	18	18	8	
Niton . .	2	8	18	32	18	8
Maximum No. of Electrons in Shell	2	8	18	32	50	72

TABLE VII.

ub-group n_k	K_{I} 1_1	L_{I} 2_1	$L_{\mathrm{II\text{-}III}}$ 2_2	M_{I} 3_1	$M_{\mathrm{II\text{-}III}}$ 3_2	$M_{\mathrm{IV\text{-}V}}$ 3_3	N_{I} 4_1	$N_{\mathrm{II\text{-}III}}$ 4_2	$N_{\mathrm{IV\text{-}V}}$ 4_3	$N_{\mathrm{VI\text{-}VII}}$ 4_4	O_{I} 5_1	$O_{\mathrm{II\text{-}III}}$ 5_2	$O_{\mathrm{IV\text{-}V}}$ 5_3	P_{I} 6_1	$P_{\mathrm{II\text{-}III}}$ 6_2
elium .	2														
eon .	2	2	6												
rgon .	2	2	6	2	6										
rypton .	2	2	6	2	6	10	2	6							
enon .	2	2	6	2	6	10	2	6	10		2	6			
iton .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6
aximum umber of ectrons Sub- oup .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6

fundamental ideas of practically all electronic theories of valency and atomic structure, in so far as the number of electrons in the outermost shell of every inert gas except helium is taken as eight.

Following upon this scheme of the grouping of the electrons in the atoms of the rare gases, we must now consider briefly the detailed stages in the building up of each outer valency shell and also the further development of inner shells of electrons in passing through each period of elements in the Periodic System. We confine ourselves to a consideration of the orbits occupied by the different electrons in each atom only in so far as these orbits are determined by the two quantum numbers n and k. Tables VI. and VII., as well as Table VIII. at the end of the Chapter, may be continually referred to in what follows.

First Period.—From spectroscopic evidence the most stable orbit of the single electron in the hydrogen atom is a 1_1 orbit. In building up the helium atom by successive additions of the two electrons to the helium nucleus, the first electron added must also assume a 1_1 orbit as the most stable configuration, and from our scheme of electron groupings in Table VI. it appears that the second added electron should be bound in an equivalent 1_1 orbit. This conclusion is supported by a consideration of the arc spectrum of helium, the largest term of which is a singlet ^1S term. The nature of this term indicates a 1_1 orbit as the normal orbit for both the extra-nuclear electrons of helium. Regarding the spatial disposition and the magnitudes of the orbits of the two electrons in the helium atom, little can be said with any degree of certainty. For the more complex structures of the other elements, the difficulties involved in the dynamical problem of computing the mutual interactions of all the extra-nuclear electrons in their orbits are, of course, such that we are forced to accept very rough pictures of these atoms, with little more than the quantum parameters of the orbits specified and very rough estimates of the dimensions of the peripheral shells. With helium, however, these difficulties should not be prohibitive, but the most exhaustive calculations have not yet resulted in any completely satisfactory model of this three-body system. In the plane model first suggested by Bohr, the two electrons were considered to revolve about the nucleus in the same circular orbit, being always diametrically opposed to one another at any instant. This model is, of course, at variance with the principle now fundamental to atomic theory that the orbits of the electrons in any atom are all separate and distinct. Apart from this, however, the structure is intrinsically unstable if the ordinary laws of mechanics and electrostatics are at all applicable, and further the model predicts too high a value for the ionisation potential of the atom, that is, the work required to strip the normal atom of one of its electrons. A model generally favoured for some time was the crossed orbit model, with the two electrons circulating round the nucleus in independent and approximately circular paths the planes of which are inclined to one another at an angle of 120°. This again is unstable and yields too low a value for the ionisation potential. In another plane model, due to Sommerfeld, the two electrons circulate in opposite directions round the nucleus in separate but co-planar and approximately elliptical paths with the nucleus as their common focus. This also fails to satisfy the ordinary criteria of mechanical stability, but it has the advantage over the previous models of predicting the correct value of the ionisation potential of helium.

Second Period.—As indicated in Tables VI. and VII., the electronic configuration of the normal helium atom persists as the internal shell of electrons for all the succeeding elements. In lithium, then, the first two electrons added to the stripped nucleus will both occupy 1_1 orbits, and from the spectroscopic evidence the normal position of the last added electron in the neutral atom is in a 2_1 orbit. This represents a much looser binding of the valency electron than the others, conforming to the ease with which the singly-ionised lithium atom is obtained. That the lithium-like structure of the first three electrons added is also maintained in all the elements which follow is borne out by a detailed analysis of the spectra of Be^+, B^{++}, C^{+++}, N^{++++}, and O^{+++++}, which are all very similar in nature to the arc spectrum of lithium itself. As regards the orbits taken up by the electrons beyond the third in the remaining atoms of the second period, the spectroscopic evidence is not complete. The divalency of beryllium, however, suggests that the third and fourth electrons in this neutral atom both occupy equivalent 2_1 orbits, and in agreement with this the spectra of B^+, C^{++}, N^{+++}, etc., show that in these ions also the last added electron occupies a 2_1 orbit. In the spectrum of singly-ionised carbon the largest term is a 2_2 term, from which it may be concluded that the 2_1 shell is completed and the 2_2 group of orbits begun by the fifth electron in neutral boron and in singly-ionised carbon. The neutral carbon atom itself probably has two of its valency electrons in 2_1 orbits and the other two in 2_2 orbits, and the development of the 2_2 group proceeds smoothly (cf. Table VIII.) with the remaining elements of the period, reaching completion in neon which has in all six electrons in this sub-group.

Third Period.—With this begins the development of the three-quantum group of orbits, the eleventh added electron to the nucleus of any of the elements from sodium onwards taking up a 3_1 orbit, as is borne out by the nature of the largest terms in the spectra of Na, Mg^+, Al^{++}, and Si^{+++}. These spectra, which correspond to the stages in the binding of the eleventh electron to the respective atom residues, are very similar to one another, and the largest term in each is a 3_1 term. The development of the 3_1 and 3_2 groups of orbits in the third period follows exactly the same course as that of the 2_1 and 2_2 groups in the preceding period. With neutral magnesium the 3_1 group is fully developed, the third valency electron of aluminium normally occupies a 3_2 orbit, and the successively added electrons in the remaining elements of the period also enter the 3_2 shell.

Fourth Period.—This is the first *long* period in the system of the elements, and, as already noted, within this period not only are the 4_1 and 4_2 groups of electronic orbits developed, but also the 3_3 group. The question of interest is to decide at what point the development of this group begins. The arc spectrum of potassium indicates a 4_1 orbit as the normal orbit of its valency electron, and the argon-like configuration of the atom residue is evidenced by the general similarity between the complex spark spectrum of potassium and the equally complex arc spectrum of argon. The arc and spark spectra of calcium show that both valency electrons of the normal calcium atom also occupy 4_1 orbits. After this comes scandium, the first of the group of eight transition elements bracketed together in the fourth column of Fig. 15. In these elements the marked gradation of physical and chemical properties which characterises the normal development of the two preceding periods of elements is interrupted. The transition elements all exhibit the property of variable valencies, they have all practically the same atomic volume, and they all (except scandium) form coloured salts which are paramagnetic. For these and other reasons which we need not detail, the group is justifiably set apart in the Periodic Classification. On the other hand, the eight elements Cu—Kr which complete the fourth period are in most respects the chemical and physical homologues of the elements in corresponding order of the periods Li—Ne and Na—A. In conformity with this, it is found from the arc spectra of the first three elements copper, zinc, and gallium that the last added electrons in copper and zinc occupy 4_1 orbits and the last added electron in gallium occupies a 4_2 orbit. Presumably the 4_2 group of electronic orbits is further developed in the remaining elements up to krypton, just as are the 2_2 and 3_2 groups in the preceding homologous series. It follows that the 3_3 group of orbits is initiated and developed in the interval between calcium and copper. The position of first appearance of a 3_3 orbit in the building up of the atoms is made clear by a detailed examination of the optical terms of the spectra of neutral potassium, singly-ionised calcium, doubly-ionised scandium, and trebly-ionised titanium. From the nature of the largest term in each of these spectra it can be inferred that, whereas a 4_1 orbit represents the most stable binding of the nineteenth electron added to the potassium nucleus or to the calcium nucleus to form K or Ca^+, the nineteenth electron added to the scandium nucleus to form Sc^{++} or to the titanium nucleus to form Ti^{+++} finds its strongest binding not in a 4_1 orbit but in a 3_3 orbit. The 3_3 group of orbits begins then in the doubly-ionised scandium ion. It should be remarked that here for the first time in the building up of the electronic configurations of the elements do we meet with structures such as neutral potassium and singly-ionised calcium on the one hand, and doubly-ionised scandium and trebly-ionised titanium on the other, which have the same number of extra-nuclear electrons, but exhibit different groupings of these electrons.

While the last electron in Sc^{++} moves in a 3_3 orbit, the further two electrons in the neutral scandium atom both occupy 4_1 orbits as in calcium. With the next element titanium we have two electrons in 3_3 orbits and two in 4_1 orbits, and spectroscopic evidence shows that either one or two electrons persist in 4_1 orbits while the 3_3 group is further developed in the remaining transition elements. The details (cf. Table VIII.) in the construction of these need not detain us. Throughout the transition group, however, the strengths of binding of electrons in 3_3 and 4_1 orbits are very little different, and it is to this fact that the variable valencies of the transition elements must be ascribed. Further, it should be noted that during the development of the 3_3 group of electrons, the spatial dimensions of the atoms are roughly determined by those of the outer 4_1 shell of orbits. Since the number of electrons in this shell remains the same for almost all of the transition elements, and since further the net positive charge within this shell remains unaltered—the increase in the number of electrons in the 3_3 group going hand in hand with increase in the positive nuclear charge—it follows that the dimensions of the outer shell of electrons should remain approximately constant throughout the group. This is in agreement with the fact that the atomic volumes of the transition elements are all very much the same in value.

The break in the normal development of the four-quantum orbits finishes at the copper atom, wherein the 3_3 group is complete with ten electrons and the electron last added to form the neutral atom occupies a 4_1 orbit. That only *nine elements*, viz. Sc—Cu, participate in the development of the 3_3 group of *ten electrons* is due to the fact that, whereas the element calcium which precedes scandium has two electrons in 4_1 orbits, the normal copper atom has only one. The functioning of copper in its chemical combinations both as a monovalent and as a divalent element and its similarity in some respects to the transition elements are due to the fact that in its electronic structure the strength of binding of a 3_3 orbit is still not very different from that of a 4_1 orbit.

Fifth Period.—Like the preceding period this contains eighteen elements, and the development from rubidium to xenon of the four- and five-quantum groups of orbits is exactly analogous to that of the three- and four-quantum groups from potassium to krypton. In krypton the 4_1 and 4_2 groups of orbits are completed, and for all succeeding elements the first thirty-six electrons attached to their nuclei adopt the krypton-like configuration. With the elements rubidium and strontium which are the chemical homologues of potassium and calcium respectively, the valency electrons do not initiate the development of the 4_3 or 4_4 groups, but, from the spectroscopic evidence, both electrons occupy 5_1 orbits. After strontium comes another group of eight transition elements very similar to the group Sc—Ni in the fourth period, and this group is followed by Ag, Cd, In, etc., which are the chemical homologues of Cu, Zn, Ga. . . . This suggests—and the conclusion is again borne out by the spectroscopic data—that the break in the normal development of the five-quantum orbits occurs at yttrium, and that in the series yttrium to silver the internal 4_3 group of electrons is completed. This done, the valency electron in the neutral silver atom does not initiate the development of the 4_4 group, but assumes a 5_1 orbit, and in the succeeding elements up to xenon the normal development of the 5_1 and 5_2 orbits is continued and completed.

Sixth Period.—Beginning with cæsium and barium which belong to the alkali metals and the alkaline earths respectively, the single valency electron of cæsium and the two valency electrons of barium normally occupy 6_1 orbits. The next element lanthanum is the chemical homologue of yttrium and scandium, from which it is inferred that with lanthanum the further development of the 6_1 quantum group is postponed, in the sense that the last added electron in the doubly-ionised lanthanum atom La^{++} finds its firmest binding in a 5_3 instead of a 6_1 orbit. The two last added electrons in the neutral lanthanum atom, however, presumably occupy 6_1 orbits. Another break in the process of atom building now appears. The next element cerium is not in its chemical properties the natural homologue of the elements zirconium and titanium, which are the second members of the preceding transition groups, but closely resembles lanthanum itself. In fact, lanthanum and cerium are the first members of the special group of rare earth elements (La—Lu) all of which are closely akin in chemical properties. The very slow gradation in the properties of these elements suggests that they all possess very similar external electronic configurations and differ only in regard to the state of development of some deep-seated group of electronic orbits within their atoms. This group, however, cannot be the 5_3 group which is initiated in lanthanum, nor can it be the 5_4 group. Electrons in these positions in the rare earths would be sufficiently near the periphery of the atoms for the discrete steps in the development of these shells to produce a much more marked gradation in valency and other properties than these elements actually exhibit. The facts seem rather to suggest that it is the 4_4 shell of electrons, which has not hitherto entered into our scheme, that is built up throughout this series of elements. In the first place, we know from the X-ray spectra of the heaviest elements that the 4_4 group of electronic orbits is completely developed somewhere within the sixth period; actually the 4_4 level first occurs as an observed X-ray term with tantalum, which lies just beyond the group of rare earth elements. Again, the group of rare earths lanthanum—lutecium comprises altogether fifteen elements. Assuming, then, that from cerium to lutecium the state of development of the outer 5_1, 5_2, 5_3, and 6_1 shells of electrons remains as in lanthanum, we have fourteen consecutive elements to represent the stages in the building up of the 4_4 shell which, as already noted in Table VII., should when completed contain just fourteen electrons. On this basis, also, the peripheral electrons (those in the 5_3 and 6_1 orbits) of the rare earth elements, which electrons determine the chemical properties, are shielded from the developing 4_4 shell by the completed 5_1 and 5_2 shells in such a way that the marked similarity existing between all these elements is naturally explained.

The assumption that the development from cerium to lutecium of the 4_4 group of electronic orbits interrupts that of the 5_3 group which was begun in lanthanum agrees well with the fact that, omitting the series Ce—Lu, the eight successive elements lanthanum, hafnium, tantalum . . . platinum form a natural group of transition elements resembling the transition group yttrium—palladium of the preceding period. Hafnium is the chemical homologue of zirconium, tantalum of niobium, tungsten of molybdenum, etc. We may conclude, then, that the 5_3 group of electronic orbits begun in lanthanum is again in course of development between hafnium and platinum, and in support of this we may remark that the 5_3 energy level occurs as an internal X-ray term (the O_{IV}-$_V$ term in Fig. 13) in the X-ray spectra of the elements from mercury onwards. The exact distribution between 5_3 and 6_1 orbits of the electrons in the atoms from hafnium to platinum is uncertain. Beyond platinum, the long period finishes with another series of eight elements (Au—Nt) which are the chemical homologues of the elements Ag—Xe in the preceding period. In all probability, then, the 5_3 group is complete with ten electrons in the gold atom. From spectroscopic evidence this atom has a single outer electron in a 6_1 orbit, and the elements from gold to niton are presumably concerned in the normal development of the 6_1 and 6_2 groups of electronic orbits.

Seventh Period.—The element of atomic number 87 which should be an alkali metal is unknown. For the next element radium, which is an alkaline earth metal, both the valency electrons are probably bound in 7_1 orbits. The four remaining elements, actinium, thorium, uranium-X, and uranium are the chemical homologues of lanthanum, hafnium, tantalum, and tungsten respectively, which suggests the development in them of the internal 6_3 shell of electrons. The detailed steps in this development are, however, uncertain. That this shell, in preference to the as yet untouched 5_4 shell, is initiated here, is shown by the failure of another group of rare earths (which would correspond to the development of the 5_4 shell) the homologues of cerium, praseodymium, etc., to appear early in the seventh period. Calculations suggest that another group of rare earths should begin in this period at about the atomic number 95.

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TABLE VIII.

TABLE OF ATOMIC STRUCTURES.

Element.	*Z*	Extra-nuclear Electronic Configurations.																							
		K	*L*		*M*			*N*				*O*					*P*						*Q*		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
H	1	1																							
He	2	2																							
Li	3	2	1																						
Be	4	2	2																						
B	5	2	2	1																					
C	6	2	2	2																					
N	7	2	2	3																					
O	8	2	2	4																					
F	9	2	2	5																					
Ne	10	2	2	6																					
Na	11	2	2	6	1																				
Mg	12	2	2	6	2																				
Al	13	2	2	6	2	1																			
Si	14	2	2	6	2	2																			
P	15	2	2	6	2	3																			
S	16	2	2	6	2	4																			
Cl	17	2	2	6	2	5																			
A	18	2	2	6	2	6																			
K	19	2	2	6	2	6		1																	
Ca	20	2	2	6	2	6		2																	
Sc	21	2	2	6	2	6	1	2																	
Ti	22	2	2	6	2	6	2	2																	
V	23	2	2	6	2	6	3	2																	
Cr	24	2	2	6	2	6	5	1																	
Mn	25	2	2	6	2	6	5	2																	
Fe	26	2	2	6	2	6	6	2																	

Ni	28	2	2	6	2	6	8	2								
Cu	29	2	2	6	2	6	10	1								
Zn	30	2	2	6	2	6	10	2								
Ga	31	2	2	6	2	6	10	2	1							
Ge	32	2	2	6	2	6	10	2	2							
As	33	2	2	6	2	6	10	2	3							
Se	34	2	2	6	2	6	10	2	4							
Br	35	2	2	6	2	6	10	2	5							
Kr	36	2	2	6	2	6	10	2	6							
Rb	37	2	2	6	2	6	10	2	6			1				
Sr	38	2	2	6	2	6	10	2	6			2				
Y	39	2	2	6	2	6	10	2	6	1		2				
Zr	40	2	2	6	2	6	10	2	6	2		2				
Nb	41	2	2	6	2	6	10	2	6	4		1				
Mo	42	2	2	6	2	6	10	2	6	5		1				
Ma	43	2	2	6	2	6	10	2	6	6		1				
Ru	44	2	2	6	2	6	10	2	6	7		1				
Rh	45	2	2	6	2	6	10	2	6	8		1				
Pd	46	2	2	6	2	6	10	2	6	10						
Ag	47	2	2	6	2	6	10	2	6	10		1				
Cd	48	2	2	6	2	6	10	2	6	10		2				
In	49	2	2	6	2	6	10	2	6	10		2	1			
Sn	50	2	2	6	2	6	10	2	6	10		2	2			
Sb	51	2	2	6	2	6	10	2	6	10		2	3			
Te	52	2	2	6	2	6	10	2	6	10		2	4			
I	53	2	2	6	2	6	10	2	6	10		2	5			
Xe	54	2	2	6	2	6	10	2	6	10		2	6			
Cs	55	2	2	6	2	6	10	2	6	10		2	6		1	
Ba	56	2	2	6	2	6	10	2	6	10		2	6		2	
La	57	2	2	6	2	6	10	2	6	10		2	6	1	2	
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1	2	
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1	2	
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1	2	
Il	61	2	2	6	2	6	10	2	6	10	4	2	6	1	2	
Sa	62	2	2	6	2	6	10	2	6	10	5	2	6	1	2	
Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1	2	

TABLE VIII (*continued*).

Element.	Z	Extra-nuclear Electronic Configurations.																							
		K	L		M			N				O					P						Q		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1			2								
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1			2								
Ds	66	2	2	6	2	6	10	2	6	10	9	2	6	1			2								
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1			2								
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1			2								
Tu	69	2	2	6	2	6	10	2	6	10	12	2	6	1			2								
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1			2								
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1			2								
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2			2								
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3			2								
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4			2								
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5			2								
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6			2								
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7			2								
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9			1								
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10			1								
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10			2								
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10			2	1							
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10			2	2							
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10			2	3							
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10			2	4							
Eka I	85	2	2	6	2	6	10	2	6	10	14	2	6	10			2	5							
Nt	86	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6							
Eka Cs	87	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6					1		
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6					2		
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	1				2		
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	2				2		
U-X	91	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	3				2		
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	5				1		

CHAPTER III.

EXCITATION POTENTIALS. ABSORPTION SPECTRA OF ATOMS. LIFE OF THE EXCITED STATE.

ENERGY DIAGRAMS.

We have already had occasion in the section on X-ray spectra to construct a diagram (cf. Fig. 14) which represents the scheme of internal energy levels corresponding to the different groups of electrons within the general atom, and upon which the various possibilities of combination of the X-ray terms and the series relations of these combinations are easily depicted. For many purposes it is convenient to have a similar picture of the different energy levels which the atom can assume through the displacement of its most loosely bound—optical—electron from its normal to virtual orbits, which energy levels correspond to the optical terms in the arc spectrum of the element. We will discuss here two types of "optical" energy diagrams in common use.

Taking the case of the sodium atom, the wave-numbers in decreasing order of magnitude of the terms of each sequence in the arc spectrum are given by *

$$\begin{array}{llll}
1^2S = 41449 & \left\{\begin{array}{l} 2^2P_1 = 24493 \\ 2^2P_2 = 24476 \end{array}\right. & 3^2D = 12276 & 4^2F = 6860 \\
2^2S = 15710 & \left\{\begin{array}{l} 3^2P_1 = 11182 \\ 3^2P_2 = 11176 \end{array}\right. & 4^2D = 6900 & 5^2F = 4390 \\
3^2S = 8248 & \left\{\begin{array}{l} 4^2P_1 = 6409 \\ 4^2P_2 = 6406 \end{array}\right. & 5^2D = 4412 & \\
4^2S = 5077 & & & \\
5^2S = 3437 & & &
\end{array}$$

The largest of these is the 1^2S term which therefore corresponds to the normal orbit of the valency electron. With the valency electron in this orbit the energy of the atom is a minimum. All the other terms of the arc spectrum represent different possible states of excitation of the atom above the normal. With a scale of wave-numbers running from top to bottom of the diagram, these various states are

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* Cf. Fowler, A., *Report on Series in Line Spectra*, Phys. Soc., London (1922).

now indicated by horizontal lines against the wave-numbers of the pertinent terms, and the vertical distance of each such level above the normal 1^2S level gives a measure of the extent of excitation corresponding. On the diagram of Fig. 16 the various possible com-

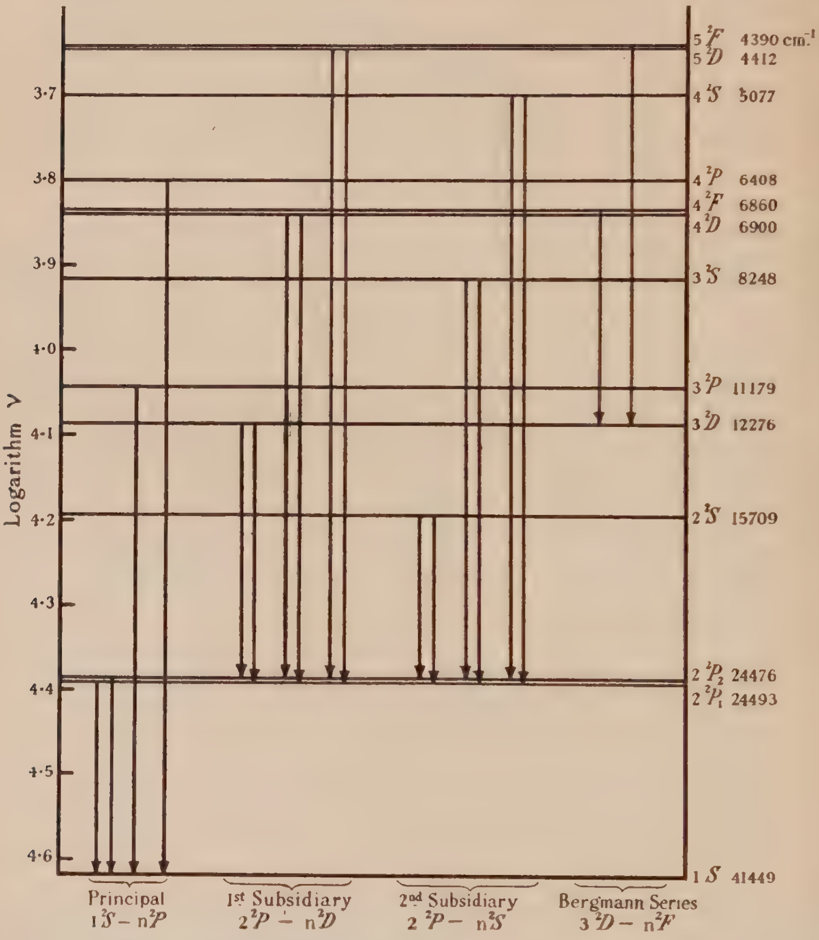

FIG. 16.—Energy diagram of sodium atom (vertical pattern).

binations of terms or energy levels associated in the production of the different spectral series (Principal, 1st Subsidiary, 2nd Subsidiary, and Fundamental) are also represented by the groups of vertical lines joining different energy levels. Without too much elaboration each such vertical line could be labelled with the wave-length of the emission to which it refers. To obtain a more open scale and a better separation of the terms of higher serial number, a logarithmic scale of wave-numbers is used in the diagram.

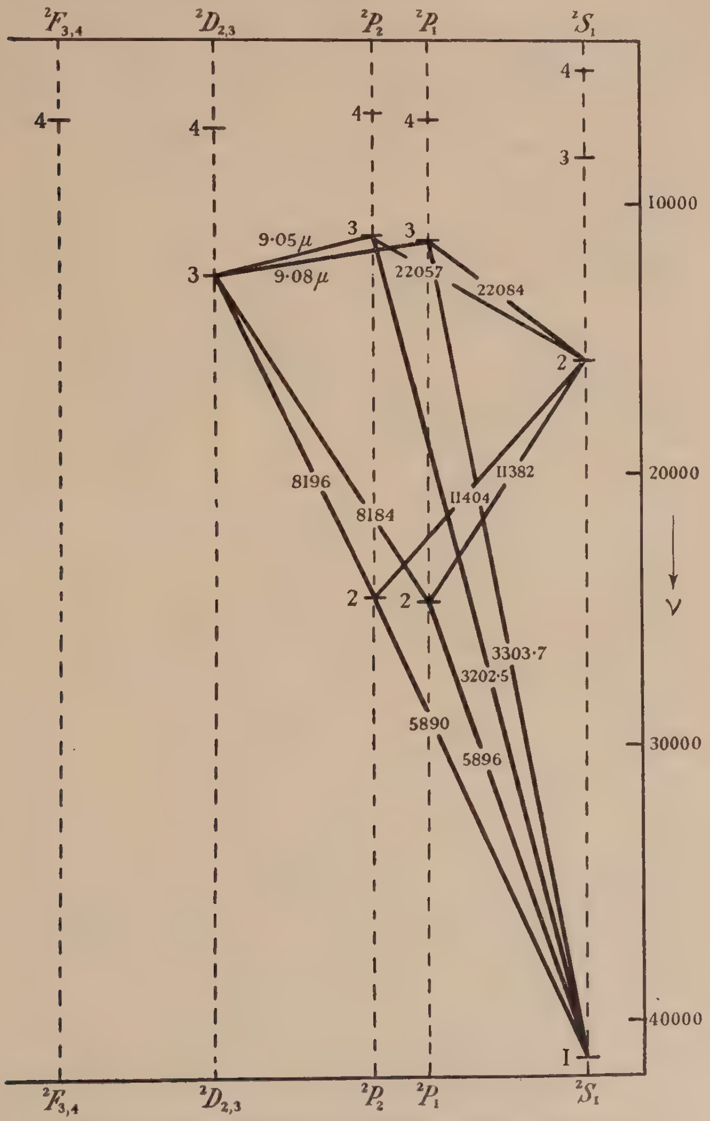

FIG. 17.—Energy diagram of sodium atom (diagonal pattern).

An alternative diagrammatic representation of the optical terms and energy levels of the sodium atom is shown in Fig. 17. Here again the wave-numbers of the optical terms are graphed vertically, but now the different sequences of terms are separated laterally in the order *S*, *P*, *D*, *F*. . . . On the *S* ordinate we mark off the points which correspond in wave-number to the 1*S*, 2*S*, 3*S* . . . terms, on the *P* ordinate the points which correspond to the 2*P*, 3*P* . . . terms, and so on. Each energy level is then given by the vertical distance

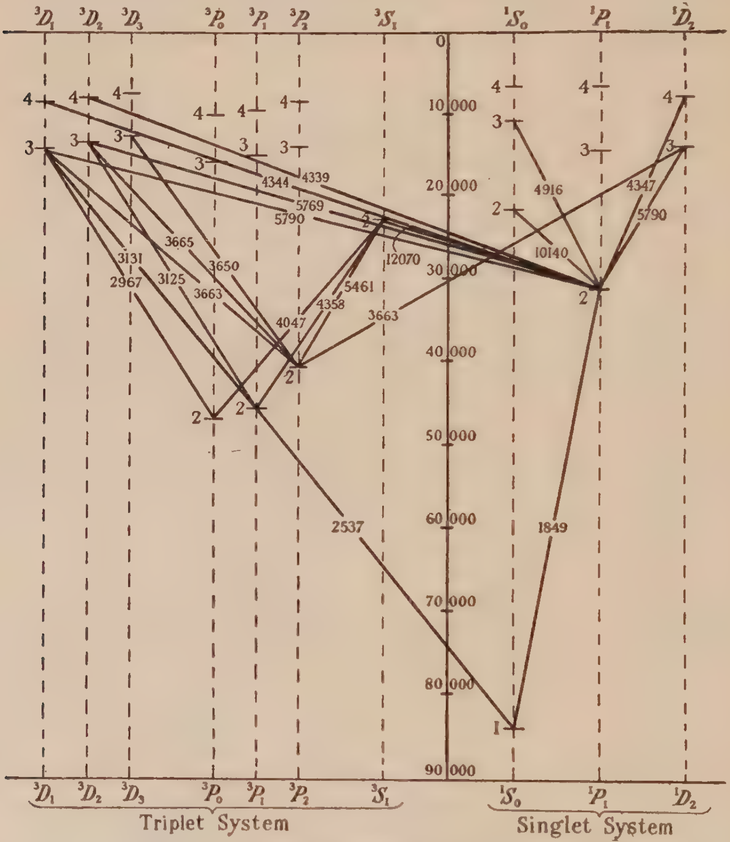

FIG. 18.—Energy diagram of mercury atom.

of the corresponding term above the lowest (1*S*) term multiplied by the factor *hc*. The transverse lines joining the different energy levels indicate the various possibilities of combination of terms to give emission lines, and each such line is labelled with the wave-length in Å of the light emitted. It is to be noted that, since terms of like character do not normally combine with one another, there are no vertical combinations in the diagram. The members of one and the same series of lines are the transverse lines which converge downwards from the various points on one ordinate to a single point on another. This latter point represents the fixed term of the series in question.

An energy diagram of the same type for the mercury atom is shown in Fig. 18 and will be found useful for future reference. In the case of mercury, the complete arc spectrum is built up from two systems of terms of different multiplicities, a singlet system ^1S, ^1P, ^1D . . . and a triplet system ^3S, ^3P, ^3D. . . . In the diagram, the energy levels of the atom corresponding to the optical terms of the two systems are for convenience represented to the right and left respectively of the wave-number axis. The transverse lines joining different energy levels again denote the emission lines actually obtained in the arc spectrum. As will be seen there are found not only singlet-singlet and triplet-triplet combinations, but also certain singlet-triplet combinations.

METASTABLE STATES OF ATOMS.

Mercury.—The normal energy level of the mercury atom corresponds to the first term 1^1S_0 of the singlet system. The next highest singlet term is the 2^1P_1, which combines both in emission and in absorption with the 1^1S_0 term to give the intense ultra-violet line of wave-length 1849 Å. However, as our energy diagram shows, the first state of excitation of the atom above the normal is not the 2^1P_1 but a 2^3P level. There are three 2^3P energy levels corresponding to the three 2^3P optical terms in the arc spectrum, but, while these levels are not very different in value, an important distinction must be drawn between the middle 2^3P_1 level and the other two. In the arc spectrum of mercury the 2^3P_1 term is found in combination with the singlet 1^1S_0 term in the well-known resonance line of wave-length 2537 Å. On the other hand, the spectral lines corresponding to the combinations $1^1S_0 - 2^3P_0$ and $1^1S_0 - 2^3P_2$ are not obtained under ordinary conditions in this spectrum, and indeed both are forbidden by the Selection Rule governing the possible changes of the inner quantum number j in emission. Again, the 2^3P_1 energy level of the mercury atom is attainable from the normal 1^1S_0 level by direct absorption of the resonance wave-length 2537 Å, yet neither of the levels 2^3P_0 and 2^3P_2 can normally be reached in mercury vapour by the simple act of absorption, in other words the reversals of the inter-orbital transitions which are forbidden in emission are likewise absent in absorption. The 2^3P_1 state of excitation of the mercury atom is termed a "labile" state. It represents an energy content of the atom far above the normal, and the atom, when raised to this state by simple absorption or by any other means, can *of itself* revert to the normal by emission of its excess energy as radiation. The 2^3P_0 and 2^3P_2 states of excitation are, however, "metastable." Although they also represent high energy contents of the atom, yet the atom when so excited is powerless to revert spontaneously to the normal state, and must for the dissipation of its excess energy depend upon collisions with other atoms, molecules, or electrons. A glance at the energy diagram for mercury shows that these two metastable states of the atom are unique. From any other energy level the atom can always pass of itself—by one or more processes of emission—to some lower energy level, either to the normal state or, at the worst, to one of the metastable states themselves.

The possession of metastable states of excitation is not of course confined to the mercury atom. The necessary criterion, that there should be optical terms other than the largest (which corresponds to the normal state of the atom) which can combine only with terms smaller in value than themselves, is fulfilled, for example, by zinc and cadmium, which give arc spectra and energy diagrams completely analogous in structure to the arc spectrum and energy diagram of mercury. It is of interest, however, to remark that the alkali metal atoms, which give arc spectra of simple doublet construction, cannot assume metastable states. This may be verified by reference to the energy diagram of sodium above, where it will be seen that each of the higher energy levels is linked up with the normal by one or more spontaneous processes of emission.

The occurrence of metastable atoms in luminescent mercury vapour is, of course, concomitant with the emission of those lines 2967 Å, 4047 Å, 5461 Å, etc., which correspond to transitions of the atom from higher S and D energy levels to the 2^3P_0 and 2^3P_2 levels. In the next Section we will discuss the production of these metastable states of excitation (among others) directly from the normal state by inelastic collisions of mercury atoms with high-speed electrons. We might here mention an interesting observation of R. W. Wood relating to the lower metastable state of the mercury atom. The energy level of this lies just below that of the labile 2^3P_1 state of excitation which is produced by absorption of the resonance line of wave-length 2537 Å, and a variety of evidence (to be dealt with in Chapter V.) points to the fact that collisions of mercury atoms in the labile 2^3P_1 state with molecules of certain foreign substances simultaneously present may induce the change represented by $\mathrm{Hg}(2^3P_1) \rightarrow \mathrm{Hg}(2^3P_0)$. In agreement with this, Wood finds that while mercury vapour, at room temperature and with or without nitrogen present, will not absorb radiation of wave-length 4047 Å, which requires the 2^3P_0 state of the atom as the initial state in the act of absorption, yet this same wave-length is very strongly absorbed when the mercury vapour, with a small amount of nitrogen present, is illuminated simultaneously with radiation of wave-length 2537 Å. The consecutive processes which obviously occur in the latter event are represented as follows :—

$$\mathrm{Hg}(1^1S_0) \xrightarrow{2537\ \text{Å.}} \mathrm{Hg}(2^3P_1) \xrightarrow{+\ \mathrm{N}_2} \mathrm{Hg}(2^3P_0) \xrightarrow{4047\ \text{Å.}} \mathrm{Hg}(2^3S_1).$$

Helium.—The case of the helium atom, the spectrum and optical energy levels of which are represented diagrammatically in Fig. 19, is of peculiar interest. The complete arc spectrum of helium, like

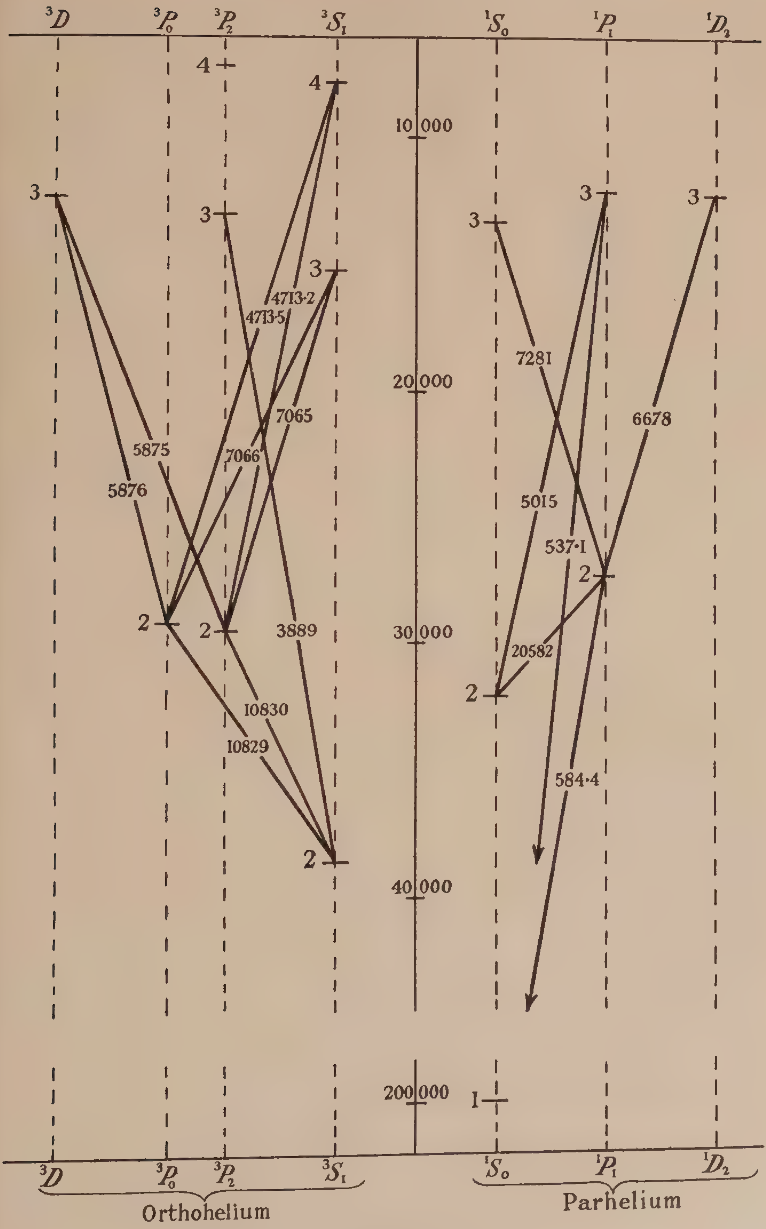

FIG. 19.—Energy diagram of helium atom.

that of mercury, is built up from two distinct systems of terms, each of which has its own S, P, D, and F sequences. As with mercury, all the terms of the one system are simple, whereas the S terms of the other system are singlets but the P, D, and F terms triplets. Until recently, indeed, the triplet system of helium terms was regarded as a doublet system on account of the vanishingly small differences between two of the components of each triplet term. Such an assumption is, however, at variance with the most modern views on the general structure of series spectra. With a singlet and a doublet system of optical terms, helium would be unique among the elements, it being a general rule that when there is more than one system of terms in the same spectrum, their multiplicities must be all odd or all even. That the actual multiplicity of the more complex of the helium systems of terms is three is also suggested indirectly by the anomalous intensity relations of certain of the apparent doublet lines in the spectrum.

The helium arc spectrum differs from that of mercury—and indeed from all other spectra which are composed of two systems of terms of different multiplicities—in regard to the possibilities of inter-combinations of terms encountered in it. The various terms of the singlet system combine normally with one another to give the emission lines of the so-called "parhelium spectrum," the terms of the triplet system also combine among themselves to give the "orthohelium spectrum," but the sole example of inter-combination which has so far been observed is the line $\nu = 1^1S_0 - 2^3P_1$ of wave-length 591·6 Å. in the extreme ultra-violet, and the very feeble intensity of emission of this line points to a very small probability of the occurrence of the electronic transition concerned. In the practical absence of inter-combination lines, we must then suppose that, under the conditions of emission of the arc spectrum of helium, two distinct modifications of the atom, orthohelium and parhelium, co-exist which are not spontaneously interchangeable. The singlet system of terms corresponds to the different possible states of excitation of parhelium, the triplet system to the various possible states of excitation of the orthohelium modification. Considering now the energy levels in the diagram of Fig. 19, the 1^1S_0 level is by far the lowest and must represent that of the normal unexcited helium atom (parhelium) with both extra-nuclear electrons occupying very stable 1_1 orbits. The first state of excitation of the atom above the normal corresponds to the 2^3S_1 (orthohelium) term, but since this does not combine with 1^1S_0 in emission, the orthohelium atom in the 2^3S_1 state can only be produced from the normal parhelium atom through the agency of collisions, and when so produced it is, in spite of its very large excess energy content, metastable. The 2^3S_1 term represents the normal state of the orthohelium atom, for which the electronic shell is usually regarded as comprising one electron in a 1_1 orbit and the other electron much less firmly bound in a co-planer 2_1 orbit. The work required to free this loosely bound electron from the atom residue is even less than that necessary to form the Li^+ or Na^+ ion from the normal lithium or sodium atom. Hence the metastable orthohelium atom, in contrast with ordinary helium, should be even more electropositive and more reactive chemically than the atoms of these alkali metals. To this fact may be ascribed the appearance of a band spectrum in helium, which points to the presence of molecular structures when the gas is electrically excited to emission at sufficiently high pressures.

The next energy level of helium above the 2^3S_1 is the 2^1S_0 level. The 2^1S_0 term also cannot combine with the fundamental 1^1S_0 term in emission, so that it must represent another metastable condition of the helium atom. The essential difference between the 2^1S_0 energy levels of mercury and helium should be noted. With mercury, the 2^1S_0 excited atom can revert spontaneously to the normal state *via* the 2^1P_1 level by two consecutive processes of emission. This possibility is, however, excluded for helium, since the 2^1P_1 level now lies above the 2^1S_0 level.

Since the only way in which the metastable helium atom can normally get rid of its excess energy is by collision with some other atom, molecule, or electron, it follows of necessity that the reverse process, the excitation of the atom to the metastable state, must also occur by collision under suitable conditions. The production of the 2^3S_1 and 2^1S_0 states of helium by collision of the normal atom with high-speed electrons is dealt with in the next Section.

RESONANCE AND IONISATION POTENTIALS.

The most direct evidence for the reality of the discrete stationary states of excitation of the atoms envisaged in Bohr's first postulate is afforded by the researches initiated by Franck and Hertz in 1913 upon the conditions of energy transfer between atoms and free electrons. Under the conditions of investigation, a stream of fast-moving electrons is passed through a monatomic gas or vapour, maintained at sufficiently low temperatures so that the atoms of the gas may be regarded as practically at rest relative to the impinging electrons. The loss of energy on the part of the electron stream is investigated in so far as this depends upon the initial velocity of the electrons and upon the nature of the atoms with which they collide.

When collision between a fast-moving electron and a stationary atom occurs, the former may lose kinetic energy in two ways :—

(1) by transfer of energy which after the impact will appear as energy of free translatory motion of the atom ;

(2) by transfer of energy which after the impact will appear as internal energy of the atom.

When in any mechanical collision energy transfer occurs only in the sense (1), we term the collision elastic ; if also in the sense (2), the collision is inelastic.

In both elastic and inelastic collisions, however, the fraction of its total translatory energy which the electron can transfer as such to the atom must always be very small. This is due to the great disparity of the masses of the colliding units. It can be shown that, under the most favourable conditions of impact, the fraction of its energy ($\frac{1}{2}mv^2$) lost by the electron of mass m and velocity v in an *elastic* collision with an atom of mass M is $2m/M$ of the whole, and for a sodium atom as the colliding partner this fraction is less than $\frac{1}{20000}$. The amount similarly transferred as free translational energy in an *inelastic* collision must be even less than this. Considering now the possibility of the internal energy of the atom being increased by the collision, the classical and the quantum theories offer two very different predictions. On the classical view, each electron in the normal atom is held in an equilibrium position by forces of a quasi-elastic nature, but can be made to vibrate about this equilibrium position with any amplitude corresponding to the continuously variable amount of energy which can be associated with each internal degree of freedom of the system. When an electron strikes the atom, the collision should always be inelastic, part of its translational energy being transformed into energy of vibration of one or more of the bound electrons, and the amount of energy thus lost by the impinging electron should increase continuously as its initial velocity or kinetic energy increases. On the basis of the hypothesis of stationary states, however, the internal energy content of the atom is only discontinuously variable. In the normal atom, each electron is supposed to move in a definite quantised orbit, and the atom can only depart from its normal to a higher energy level through the removal of one or other of the electrons from its normal orbit into another quantised orbit. If then the impinging electron possesses sufficient or more than sufficient kinetic energy to effect the inter-orbital transition, the energy transfer from electron to atom *may* take place, in which case the collision will be inelastic. As long, however, as the kinetic energy of the electron falls short of that of the lowest excitation level of the atom, the collision must be elastic and the electron must rebound from the atom with unaltered velocity.

In confirmation of the quantum concept of discrete internal energy levels, it is indeed found that when high-speed electrons pass through a monatomic gas or vapour (the atoms of which have no electron affinity) there are certain well-defined critical velocities of the electrons at which large transfers of energy take place between them and the atoms, and below the lowest of which critical velocities the collisions are perfectly elastic. One of Franck and Hertz's methods of detecting and measuring these critical velocities may be briefly described.

Measurement of Critical Potentials.—A constant stream of slow-moving electrons is supplied by thermionic emission from the heated filament A. The filament is surrounded by the cylindrical gauze B, and this in turn by the concentric plate D which connects through the galvanometer G to earth. The space between A and D is filled at fairly low pressure with the gas or vapour under examination. The electron stream in traversing the space between A and B passes through a variable accelerating potential difference V_1, and from B to D through a small fixed retarding potential difference V_2 (about 0·5 volt). With gradually increasing potential difference V_1 between A and B, the current which flows from plate D to earth is measured by the galvanometer. Virtually this current measures as a function of the accelerating potential V_1 that fraction of the electrons which, having passed through the accelerating field and collided with atoms in the space AB, still possess kinetic energy sensibly different from zero, in other words, sufficient velocity at B to carry them through the small retarding field between B and D.

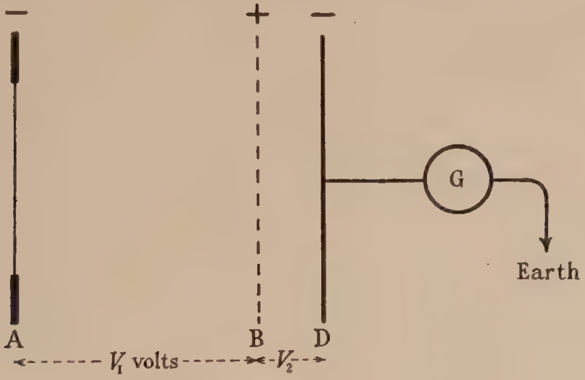

FIG. 20.

In passing freely between two points of potential difference V, an electron acquires kinetic energy in amount given by

$$\frac{1}{2}mv^2 = \frac{Ve}{300} \text{ ergs,}$$

where V is expressed in volts and e, the charge of the electron, in electrostatic units (equals $4{\cdot}775 \times 10^{-10}$ e.s.u.). From this relation is derived the useful convention of specifying the velocity or kinetic energy of the electron (or indeed any energy) in terms of volts. When we say that an electron has a velocity or kinetic energy of V volts, we mean that it has that velocity or kinetic energy which it would acquire in falling from rest through an accelerating field of V volts. Now the average initial velocity of the electrons as they leave the filament A may be taken as negligible compared with the velocity they acquire in falling through the field V_1. Accordingly, electrons which reach the gauze B without having suffered any but elastic collisions *en route* have each acquired kinetic energy equivalent to V_1 volts. If $V_1 < V_2$, this energy is lost by electrical retardation before the electrons reach the plate D, and no current flows through the galvanometer. The current begins as soon as V_1 exceeds V_2, and, so long as the accelerated electrons suffer only elastic collisions with the atoms of the gas or vapour, it increases progressively as V_1 increases. When, however, the potential V_1 reaches a critical value V_c such that the accelerated electron, when contiguous to B and with a velocity equivalent to V_c volts, suffers an inelastic collision with an atom of the gas, a sharp falling off of the current is noted. This is due to the fact that the electron loses all its kinetic energy as a result of the collision and can no longer reach the plate D through the small retarding field V_2. Increasing the potential V_1 beyond this first critical value, the current again begins to increase since the electron now suffers the inelastic collision and loses its whole velocity at some distance from the gauze B, and, being still subject to the accelerating field, it re-acquires sufficient velocity before it reaches B to enable it to penetrate to the plate D. The gradual increase of current with V_1 continues until a second critical value $V_1 = 2V_c$ is reached, at which point each electron suffers two inelastic collisions with atoms between A and B, the first halfway between A and B when the electron has first attained the critical velocity V_c volts, the second contiguous to B where it again possesses this critical velocity. Accordingly, the current again falls abruptly, then gradually increases again with increasing V_1, falls again at the critical potential $V_1 = 3V_c$, and so on.

Results illustrating this behaviour with mercury vapour as obtained by Franck and Hertz are shown in Fig. 21. As will be seen the current drops abruptly at successive critical values of V_1 which are multiples of 4·9 volts.

The value 4·9 volts is termed an excitation or resonance potential of the mercury atom. Expressed in energy units, it represents the difference between the energy levels of the atom in its normal state and in the state of higher internal excitation brought about by the inelastic collision. What this latter state of excitation is follows from a calculation of the wave-length or frequency of the radiation, a quantum of which would be equivalent to an energy of 4·9 volts. When this calculation is effected by means of the relation

$$\frac{Ve}{300} = h\nu = \frac{hc}{\lambda},$$

it transpires that the wave-length of radiation equivalent to the excitation potential 4·9 volts is practically equal to that wave-length 2536·7 Å which represents the principal line in the arc spectrum of mercury. This is the line $\nu = 1^1S_0 - 2^3P_1$ emitted by the mercury atom when the radiating electron passes from the 2^3P_1 level to its normal 1^1S_0 level. We see, then, that the effect of the inelastic collision between the electron of kinetic energy 4·9 volts and the atom is to bring about the inter-orbital transition $1^1S_0 \rightarrow 2^3P_1$ of the radiating electron.

Provided the mercury atom after being raised to the 2^3P_1 level by the inelastic collision is not immediately deactivated by collision with other atoms or electrons, its excess energy should be emitted as radiation of wave-length 2536·7 Å. In agreement with this expectation, Franck and Hertz found that when the atoms in mercury vapour *at low pressures* are bombarded with high-speed electrons of gradually increasing velocity, the mercury resonance line 2536·7 Å flashes out as soon as the accelerating potential applied to the electron stream reaches 4·9 volts. This observation is as significant in relation to Bohr's second postulate as is the observation of the critical potentials of the atoms in proving the real existence for them of stationary energy levels above the normal.

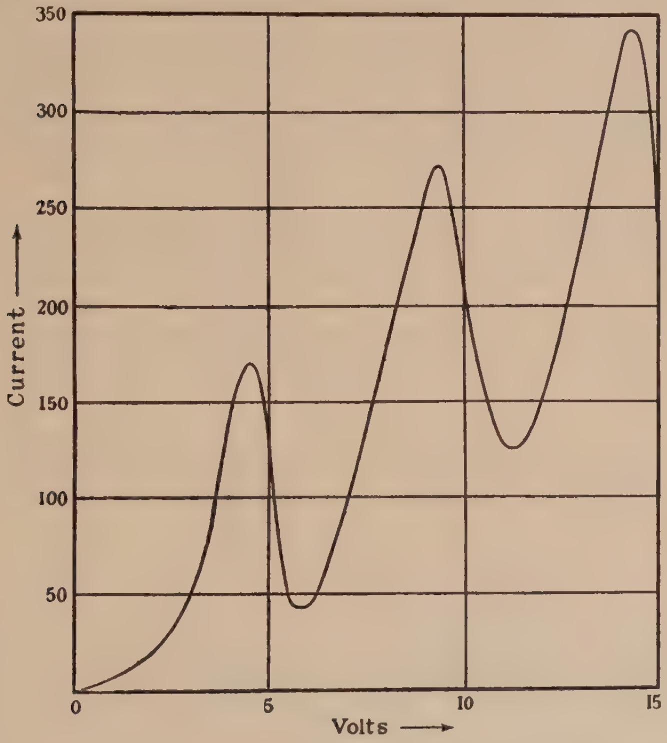

FIG. 21.—Results of Franck and Hertz for mercury vapour.

For many other elements besides mercury, the atoms when excited by inelastic collisions with high-speed electrons return to the normal state by emission of their excess energy in the form of radiation. Depending upon this fact an alternative method to the one already described is available for the study of critical potentials. With gradually increasing velocity of the incident electron stream, the first emission of radiation may be detected spectroscopically or by use of a suitable photoelectric cell.

From a glance at the energy diagram of mercury in Fig. 18, it will be seen that there are a great number of optical energy levels of the atom, besides the 2^3P_1, which the atom should equally well attain through electron impact; indeed the 2^3P_1 level does not itself represent the lowest possible state of excitation of the atom. There is no indication of these other levels in the curve of Fig. 21, the maxima of which correspond to the single resonance potential of 4·9 volts. To obtain the other excitation potentials of the atom, certain modifications of the original method of Franck and Hertz are necessary, in particular, the accelerating potential difference by which the electron stream acquires its velocity must operate upon the electrons not *while* but *before* they traverse the mercury vapour. The necessity for this precaution is obvious when we desire to work with electrons of velocity greater than 4·9 volts.

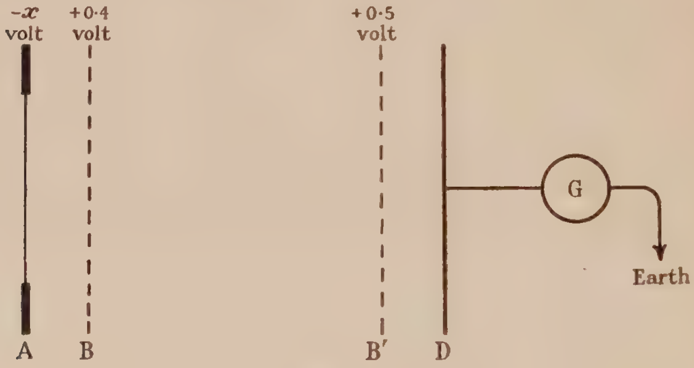

Fig. 22.

When the accelerating potential is applied gradually to the electron over its whole path through the mercury vapour, as in the original investigation of Franck and Hertz, the velocity of the electron cannot, except at very low working pressures of the vapour, exceed the first main critical value of 4·9 volts without the electron almost immediately suffering an inelastic collision which reduces its velocity to zero again. This restriction on the velocity attainable by the impinging electrons is avoided by the experimental arrangement shown in Fig. 22. Here the accelerating potential is applied to the electron stream in two stages, the bulk of the potential gradient lying between the filament A and the first gauze B. These are separated by only a very short distance, and the working pressure of the mercury vapour is low enough (0·4 mm. Hg or less) to allow a considerable fraction of the accelerated electrons to reach the gauze without colliding at all with mercury atoms. These electrons, having gained through the first fall of potential a velocity of approximately the required value, pass through the gauze B into the much larger space BB′. In traversing this they are subject to a further small accelerating potential of 0·1 volt, and suffer many collisions with mercury atoms. The electrons which reach the second gauze B′ are now subject to a small retarding potential (0·5 volt) and as before the fraction which reaches the plate D with velocity sensibly different from zero is measured electrically. By plotting the current to earth against the variable total accelerating potential ($x + 0{\cdot}5$) volts, the breaks in the curve give the successive critical potentials at which fresh possibilities of inelastic collisions between the electrons and the mercury atoms enter. Alternatively, by application of optical methods the various accelerating potentials which result in the emission of the characteristic lines of mercury in the space BB′ may be measured.

Critical Potentials of Mercury.—By methods such as these, Franck and Einsporn have made a very complete investigation of mercury vapour, and have detected as many as eighteen different critical potentials of the mercury atom. While a few of these cannot be interpreted with certainty, the majority, when expressed in energy units, agree in value with the work required to excite the mercury atom from the normal 1^1S_0 state to one or other of the states of higher energy content indicated in Fig. 18. The extent of agreement is shown in Table IX., where the values of a few of the observed critical potentials are compared with the values calculated from the differences of the optical terms in the last column. The observed critical potentials at 4·68 and 5·47 volts are of special interest, corresponding as these do to the excitation by electronic impact of the two metastable states 2^3P_0 and 2^3P_2 of the mercury atom. In relation to these it should be remarked that while such inelastic collisions evidently do occur, investigations on the readiness with which different quantum jumps can be induced by electronic impact suggest that in general such transitions as $1^1S_0 \rightarrow 2^3P_0$, which are not permitted in absorption, are also relatively difficult to produce through the medium of collision.

TABLE IX.

Critical Potentials in Mercury Vapour.

Observed Critical Potential.	Calculated Critical Potential.	Quantum Transition Concerned.
4·68 volts	4·66 volts	$1^1S_0 \rightarrow 2^3P_0$
4·90 ,,	4·86 ,,	$1^1S_0 \rightarrow 2^3P_1$
5·47 ,,	5·43 ,,	$1^1S_0 \rightarrow 2^3P_2$
6·73 ,,	6·67 ,,	$1^1S_0 \rightarrow 2^1P_1$
7·73 ,,	7·69 ,,	$1^1S_0 \rightarrow 2^3S_1$
8·86 ,,	8·79 ,,	$1^1S_0 \rightarrow 3^1P_1$
	8·81 ,,	$1^1S_0 \rightarrow 3^3D$
10·38 ,,	10·39 ,,	$1^1S_0 \rightarrow Hg^+ +$ electron

In the above table, besides the critical potentials corresponding to various states 2^3P_0, 2^3P_1, etc. of excitation of the atom, there is one at 10·38 volts equal in value to the basic term 1^1S_0 itself. Since the value of any spectral term, multiplied by *hc*, equals the work required to effect the removal of the radiating electron from the orbit which the term specifies to infinity, it is clear that this particular critical potential corresponds to an inelastic collision between impinging electron and normal atom whereby one of the valency electrons is completely ejected from its normal orbit and the atom is ionised. The critical potential at 10·38 volts is accordingly termed the *ionisation potential* of mercury. There is a second ionisation potential observed for mercury at about 20 volts which presumably corresponds to the complete ejection of *both* valency electrons from the atom, leaving the Hg^{++} residue. The atoms of zinc and cadmium have also got two ionisation potentials. For zinc, the observed values are 9·5 and 18·2 volts as compared with 9·35 and 17·9 volts calculated from the values of the basic terms of the arc and spark spectra respectively. For cadmium, the observed ionisation potentials are 9·0 and 17·3 volts as compared with the calculated figures of 8·95 and 16·84 volts.

Helium.—The critical potentials of neutral helium are of interest in relation to the different energy levels of the atom which the orthohelium and parhelium spectra predict. As is seen from Table X., there is complete accord between the spectroscopic energy levels and those measured by the method of electronic impact.

TABLE X.

CRITICAL POTENTIALS OF HELIUM.

Observed Critical Potential.	Calculated Critical Potential.	Quantum Transition Concerned.
19·75 volts	19·77 volts	$1^1S \rightarrow 2^3S$
20·55 ,,	20·55 ,,	$1^1S \rightarrow 2^1S$
21·2 ,,	21·12 ,,	$1^1S \rightarrow 2^1P$
22·9 ,,	22·97 ,,	$1^1S \rightarrow 3^1P$
24·6 ,,	24·5 ,,	$1^1S \rightarrow He^+ +$ electron

The observed critical potential at 24·6 volts is the first ionisation potential of the helium atom. A second ionisation potential has been observed for helium at 79·5 volts which corresponds to the complete ejection of both electrons from the atom.

Other Monatomic Vapours.—The resonance and ionisation potentials of a number of the elements (which give monatomic vapours) in the first two columns of the Periodic Classification are tabulated below. In making a comparison between the observed values and those calculated from the spectroscopic data a reasonable amount of latitude must of course be allowed, since the observation of a critical potential usually involves a possible experimental error of as much as a few per cent. of the voltage measured. In cases where more than one value is recorded in the literature, the figure in the last column represents the mean of the available observations.

TABLE XI.

Resonance and Ionisation Potentials of Certain Elements in the First and Second Columns of the Periodic System.

Element.	Quantum Transition.	Wave-number Difference of Terms.	Critical Potentials.	
			Calc.	Obs.
Na . .	$1S \rightarrow 2^2P_2$	16956	2·09	2·12
	$1S \rightarrow 2^2P_1$	16974		
	$1S \rightarrow \mathrm{Na}^+ + \ominus$	41449	5·12	5·15
K . .	$1S \rightarrow 2^2P_2$	12985	1·61	1·59
	$1S \rightarrow 2^2P_1$	13043		
	$1S \rightarrow \mathrm{K}^+ + \ominus$	35006	4·31	4·25
Rb . .	$1S \rightarrow 2^2P_2$	12579	1·57	1·6
	$1S \rightarrow 2^2P_1$	12817		
	$1S \rightarrow \mathrm{Rb}^+ + \ominus$	33685	4·16	4·1
Cs . .	$1S \rightarrow 2^2P_2$	11178	1·41	1·48
	$1S \rightarrow 2^2P_1$	11732		
	$1S \rightarrow \mathrm{Cs}^+ + \ominus$	31407	3·88	3·9
Cu . .	$1S \rightarrow 2^2P_2$	30535	3·78	—
	$1S \rightarrow 2^2P_1$	30783		
	$1S \rightarrow \mathrm{Cu}^+ + \ominus$	62306	7·69	7·8
Ag . .	$1S \rightarrow 2^2P_2$	30472	3·70	3·1
	$1S \rightarrow 2^2P_1$	29551		
	$1S \rightarrow \mathrm{Ag}^+ + \ominus$	61093	7·54	(6·0)
Mg . .	$1^1S \rightarrow 2^3P_1$	21870	2·70	2·65
	$1^1S \rightarrow 2^1P_1$	35050	4·32	4·42
	$1^1S \rightarrow \mathrm{Mg}^+ + \ominus$	61663	7·61	7·9
Ca . .	$1^1S \rightarrow 2^3P_1$	15210	1·88	1·90
	$1^1S \rightarrow 2^1P_1$	23652	2·92	2·85
	$1^1S \rightarrow \mathrm{Ca}^+ + \ominus$	49305	6·08	6·01
Zn . .	$1^1S \rightarrow 2^3P_1$	32501	4·02	4·14
	$1^1S \rightarrow 2^1P_1$	46744	5·77	5·65
	$1^1S \rightarrow \mathrm{Zn}^+ + \ominus$	75759	9·35	9·4
Cd . .	$1^1S \rightarrow 2^3P_1$	30655	3·78	3·91
	$1^1S \rightarrow 2^1P_1$	43691	5·39	5·35
	$1^1S \rightarrow \mathrm{Cd}^+ + \ominus$	72533	8·95	8·96
Hg . .	$1^1S \rightarrow 2^3P_1$	39412	4·86	4·9
	$1^1S \rightarrow 2^1P_1$	54069	6·67	6·7
	$1^1S \rightarrow \mathrm{Hg}^+ + \ominus$	84182	10·39	10·3

ABSORPTION SPECTRA OF MONATOMIC VAPOURS.

The reciprocal nature of emission and absorption of radiation and the quantum interpretation of the former imply that every elementary process of emission on the part of an atom must have its counterpart in absorption under suitably chosen conditions. It follows, of course, that the absorption spectrum of a system of atoms must be a line spectrum and that each absorption line must be capable of expression as the difference of two terms, the one term corresponding to the pre-absorption state of the atom, the other to the state of excitation which results from the act of absorption. Further, the restriction principles which limit the possibilities of combination of terms in emission must operate also in absorption; accordingly, from an incident homogeneous beam of radiation the atom can normally absorb only those frequencies which correspond to transitions of the atom between states the azimuthal quantum numbers of which differ by ± 1 and the inner quantum numbers of which differ by 0 or ± 1.

Absorption by Normal Atoms.—It has already been pointed out that a system of similar atoms, maintained under such conditions that all or practically all of them are in the same initial state (whether excited or unexcited), should give an absorption spectrum of very simple structure—a series of absorption lines representing in their wave-lengths the reversals of the lines of one of the optical emission series of the atom in question. The absorption spectra of the alkali metal vapours, as observed under ordinary circumstances, afford an illustration of this point. The normal state of lowest internal energy content of the alkali metal atom corresponds to the 1^2S term of its arc emission spectrum, and this is the state in which the great majority of the atoms in the metal vapour must persist over a very considerable temperature range from ordinary temperatures upwards. The first state of excitation of the atom above the normal is the 2^2P_1 state, which, in the case of sodium, represents an excess internal energy content of 2·1 volts or 48,000 calories per gram-atom.* In order to maintain any appreciable fraction of the atoms in this condition in the absence of electrical excitation or radiation, a high degree of thermal agitation of the atoms is necessary, since internal excitation of the atoms can then result only through collisions between atoms which have energy of relative translatory motion in excess of 2·1 volts. At room temperatures the number of such collisions is altogether negligible; at 500° C. the fraction of collisions for which the energy of relative motion exceeds 2·1 volts is only 10^{-12}, and at 1000° C. only 10^{-7} of the total. Accordingly, we may conclude that in sodium vapour at moderate temperatures every absorbing atom starts from the normal 1^2S state. The 1^2S term, however, combines only with the ^2P sequence of doublet terms in radiation processes, and hence the absorption spectrum should consist simply of a series of doublets, converging towards the ultra-violet and occupying the positions of the lines of the Principal Series $\nu = 1^2S - \mathrm{n}^2P_{1,2}$ of the arc emission spectrum of sodium. This is, in fact, what has been experimentally observed, first for sodium vapour by R. W. Wood (*Phil. Mag.*, [vi], **18,** 530, 1909), and later for potassium, rubidium, and cæsium vapours by Bevan (*ibid.*, **19,** 195, 1910) and Datta (*Proc. Roy. Soc.*, **101**A, 539, 1922). Working with a long column of sodium vapour at low saturation pressures, Wood found that the absorption spectrum consisted solely of the first few members of the Principal Series of lines, beginning with the D doublet at 5890-5896 Å. The absorption lines are narrow and sharply defined, and their doublet structure is well in evidence. If the pressure (saturation) of the sodium vapour be gradually increased by raising the temperature, a large number of the higher members of the series up to n = 58 can be separately identified in the absorption—a very much greater number of lines of the Principal Series, indeed, than is ever encountered in emission.

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* 1 volt is equivalent to 23,070 calories per gram-atom. This is the kinetic energy which N electrons (N = Avogadro Number) would acquire in falling through a potential difference of 1 volt.

The further members of the series $\nu = 1^2S - n^2P$ beyond n = 58 and right up to the convergence frequency $\nu = 1^2S$ itself are also absorbed by the sodium vapour, but the rapid convergence of the lines in this region, combined with the broadening of the absorption lines at the high pressures required for the detection of absorption of the higher members (the intensity of absorption falls off progressively

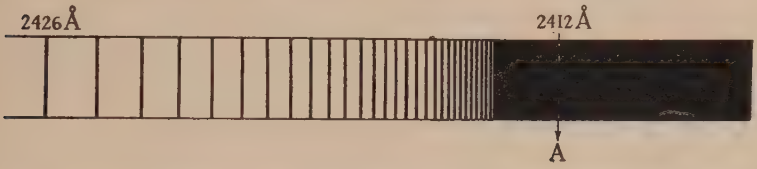

FIG. 23.—Absorption spectrum of sodium vapour in the neighbourhood of the convergence limit.

from the D line towards the convergence frequency), produces the appearance of a continuous region of absorption from the position of the n = 58 line onwards. This pseudo-continuous absorption continues as far as 2412 Å, which is the convergence position of the Principal Series of sodium, but absorption does not stop short here. Rather, there begins at the convergence limit a region of *true* continuous absorption which proceeds some distance further into the ultra-violet. The upper (short wave-length) part of this absorption spectrum is illustrated diagrammatically in Fig. 23, in which the shaded region to the right of the convergence limit A represents the true continuous absorption. Continuous absorption of the same character is observed in the cases of the other alkali metal vapours.

While the absorption lines to the left of A correspond to the passage of the valency electron of the atom from its normal orbit to outer virtual orbits, the convergence frequency and any frequency beyond this in the region of true continuous absorption must correspond to complete detachment of this electron from the atom residue. In fact, in absorption at and beyond A, we must be dealing with a photoelectric effect in the alkali metal vapour. A definite proof of the occurrence of photo-ionisation in a stationary column of alkali metal vapour illuminated with radiation of frequency above the value 1^2S is difficult, owing to the possibility of occurrence of a secondary photoelectric effect at the metal electrodes which must be introduced into the vapour to detect the presence of ions or electrons. By transverse illumination of a jet of vapour, however, and measurement of its electrical conductivity beyond the range of illumination, Williamson (*Phys. Rev.*, **21,** 107, 1923) and Samuel (*Z. Physik*, **29,** 209, 1924) have been able to demonstrate that a true photo-ionisation of potassium vapour is produced by radiation of wave-length in the neighbourhood of the convergence limit 2856 Å. In a more recent publication, Foote and Mohler (*Phys. Rev.*, **26,** 195, 1925), using a different method of investigation, have obtained a similar photoelectric effect in cæsium vapour illuminated with monochromatic radiation of frequency above that of the convergence limit ($\lambda = 3184$ Å) of the line absorption spectrum of cæsium vapour. These workers further find (*ibid.*, **27,** 37, 1926) that photo-ionisation of the cæsium vapour occurs also, although to a smaller extent, as a result of illumination with radiation of certain frequencies *below* the convergence limit. In the plot of photo-ionisation against illuminating frequency, definite maxima occur at the points corresponding to the frequencies $\nu = 1^2S - 5^2P$, $\nu = 1^2S - 6^2P$, . . . $\nu = 1^2S - 10^2P$ of the lines in the absorption spectrum of the vapour. Here, obviously, we cannot be dealing with ionisation of the cæsium atom in one elementary act of absorption, since the quantum of energy corresponding to any of these frequencies is insufficient to detach the valency electron completely from the atom residue. The cæsium atom, however, is raised to a very high energy level by absorption of any of the indicated frequencies, and, while in the excited state, it may then receive the small amount of additional energy necessary for its ionisation by collision with other atoms, or more probably, as Franck and Jordan point out, by collision with electrons of moderately high velocity, which are also present under Foote and Mohler's experimental conditions.

At moderate temperatures—200° to 500° C.—and the saturated vapour pressures corresponding, the complete absorption spectrum of any one of the alkali metal vapours contains not only the lines of the Principal Series characteristic of the atom, but also one or more series of absorption *bands* which indicate the presence in the vapour of molecules as well as atoms. Molecular bands of the same general structure occur in the spectrum of the chemiluminescence emitted by certain reacting systems which contain alkali metal vapours, and also in the fluorescence emitted by these metal vapours at moderately high vapour densities when illuminated with white light. The available evidence goes to prove that these emission and absorption bands are due to diatomic alkali metal molecules and not to accidental impurities in the vapour. The band absorption of sodium vapour has been extensively studied by Wood and collaborators. With carefully purified sodium vapour, saturated at about 300° C., there appear in the visible absorption, besides the D lines in the yellow, two systems of channelled bands, the stronger of which lies in the blue-green (460-550 $\mu\mu$), the weaker in the red (600-700 $\mu\mu$) on the long wave side of the D doublet. In the ultra-violet, also, in the neighbourhood of the second doublet of the Principal Series (3303 Å) lies another system of absorption bands, and Wood has observed that several of the succeeding members of the line absorption series carry with them similar attendant bands. The close association in spectral position of the absorption bands with the atom absorption lines suggests that for the Na_2 molecule which is responsible for the band absorption, the electronic orbits within each bound sodium atom are practically the same as in the free atom, and that, in spite of the chemical combination, what was the valency electron of the free atom is, in the molecule, still capable of occupying much the same type of virtual orbits by absorption. In this respect the presumably not too stable sodium molecule differs from such molecules as those of oxygen or chlorine for which the possible states of excitation bear no relation to those of the free atoms. Among other workers, McLennan and Ainslie (*Proc. Roy. Soc.*, **103**A, 304, 1923) have investigated the band absorption of potassium, rubidium, and cæsium vapours. With potassium, as with sodium vapour, there are, besides a series of strong channelled absorption bands in the region 650 $\mu\mu$, a series of fine channellings in the red and near infra-red on the long wave side of the first Principal doublet of potassium at 7699-7665 Å, and, at high vapour pressures, a further channelling in the neighbourhood of the second Principal doublet at 4273 Å. With rubidium and cæsium vapours there is no evidence of absorption bands appended to the long wave-length side of the absorption lines of the Principal Series, but in both cases a series of well-defined bands lie between the first and the second doublets. These band systems of the alkali metal vapours will be further referred to in the Chapter on *Fluorescence*.

The absorption spectra of the other monatomic metal vapours at temperatures below incandescence bear out, in their general features, the results obtained with the alkali metals. For the metals of Group II of the Periodic Classification, the normal state of the atom corresponds to the basic 1^1S term of its arc spectrum, and the atom should therefore absorb from a continuous spectrum radiation of frequencies given by $\nu = 1^1S - n^1P$ and also $\nu = 1^1S - n^3P_1$. In agreement with this, magnesium vapour at moderate temperatures absorbs the lines $\nu = 1^1S - 2^1P$, $1^1S - 3^1P$, and $1^1S - 2^3P_1$ of its emission spectrum, while calcium, strontium, and barium vapours each absorb several of the first members of their Principal Singlet Series $\nu = 1^1S - n^1P$. In zinc, cadmium, and mercury vapours at low pressures, the frequencies $\nu = 1^1S - 2^1P$ and $\nu = 1^1S - 2^3P_1$ are both strongly absorbed. For these elements, the higher members of these series lie outside the convenient range of spectral observation. In all cases, the absorption lines broaden considerably with increasing temperature and consequent increasing saturation pressure of the metal vapour (the same broadening is observed with the absorption lines of the alkali metal vapours), and at the same time absorption bands make their appearance which are more or less closely associated in spectral position with the series absorption lines.

The absorption spectra of the vapours of gallium, indium, and thallium present features of special interest. For each of these elements the basic, that is, the largest term of the arc emission spectrum is not an S but a P term.* In contrast then with the metal vapours of Groups I and II of the Periodic System, the vapours of gallium, indium, and thallium should absorb at the frequencies not of the Principal but of the First and Second Subsidiary Series, $\nu = 2P - \mathrm{n}D$ and $\nu = 2P - \mathrm{n}S$. The fundamental $2P$ term is, however, actually a doublet (the spectral terms for these elements belong to doublet systems), the largest component 2^2P_1 of which connotes the normal orbit of the optical electron, while the smaller component 2^2P_2 corresponds to a *metastable* activated state of the atom. The amount of excess internal energy associated with each metastable atom is shown in the table following:—

TABLE XII.

Element.	$2^2P_1 - 2^2P_2$	
	Volt.	Calories/Gram-atom .
Ga . . .	0·10	2,310
In . . .	0·27	6,230
Tl . . .	0·96	22,160

The question now arises under what conditions lines should be observed in the absorption spectrum of the metal vapour originating in the metastable state of the atom. The atom can be brought to the metastable energy level by thermal excitation; at any temperature the conditions of statistical equilibrium require that the ratio of the number of atoms possessing an excess internal energy content of E calories to the number of normal atoms should be given by $e^{-E/RT}$. This fraction is the larger the smaller E is and the higher the absolute temperature T. Accordingly, at comparatively low temperatures practically all the vapour atoms exist in the normal 2^2P_1 state and the absorption spectrum of the vapour should contain only lines of the *partial* series $\nu = 2^2P_1 - \mathrm{n}^2D_2$ and $\nu = 2^2P_1 - \mathrm{n}^2S$. With increasing temperature, however, the number of atoms maintained by thermal excitation in the 2^2P_2 state increases rapidly, and the absorption spectrum of the vapour should then also contain the lines of the other partial series $\nu = 2^2P_2 - \mathrm{n}^2D_{2,3}$ and $\nu = 2^2P_2 - \mathrm{n}^2S$. Grotrian's observations (*Z. Physik*, **12**, 218, 1922; **18**, 169, 1923) on the absorption of gallium, indium, and thallium vapours are in agreement with these conclusions. With thallium vapour, the first lines

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* Corresponding to the fact that the normal orbit of the last added electron in the neutral atom is a $k = 2$ orbit.

$\nu = 2^2P_1 - 3^2D_2$ ($\lambda = 2768$ Å) and $\nu = 2^2P_1 - 2^2S$ ($\lambda = 3776$ Å) of the two Subsidiary partial series are absorbed at the saturation pressure corresponding to 400° C.; at 500°-600° C. further absorption lines of these same partial series are observed in the far ultra-violet. With further increase in temperature all these lines are markedly broadened in absorption, but no other absorption lines appear until the temperature reaches 800° C., when for the first time the well-known green thallium line $\lambda = 5350$ Å, which corresponds to the transition $2^2P_2 \rightarrow 2^2S$, appears in the absorption spectrum. At higher temperatures (and saturated vapour pressures) a number of other members of the partial series $\nu = 2^2P_2 - n^2S$ and also several of the doublets $\nu = 2^2P_2 - n^2D_{2,3}$ are absorbed. At 800° C. where absorption by the metastable atom is first perceptible, the fraction of the thallium atoms which are maintained by the temperature in the metastable condition works out to about 10^{-4}. For indium vapour, the lines of the partial series originating in the 2^2P_1 state are first appreciably absorbed at 650° C., and those involving absorption by the metastable atom at 800° C. For gallium vapour, the corresponding temperatures are about 850° and 900° C. In agreement with theory and corresponding to the very different values of the excess energy content of the metastable atoms, the temperature difference in the appearance of absorption lines from the 2^2P_1 and the 2^2P_2 levels is least for gallium (about 50° C.) and greatest for thallium (about 400° C.).

Absorption by Excited Atoms. Thermal Excitation.—For the occurrence of absorption lines characterising excited atoms it is, of course, necessary to maintain by some means an appreciable stationary concentration of the excited atoms in the metal vapour. This can be accomplished either by thermal means, or by the passage of an electric discharge through the vapour, or by sufficiently intense illumination of the vapour with radiation of suitable quality which the *normal* atoms can absorb.

We have just dealt with the circumstances under which gallium, indium, and thallium vapours can absorb lines characteristic of their metastable atoms, the necessary concentration of such atoms in the vapour being maintained by temperature. As a further example, the absorption of thermally excited potassium vapour may be mentioned. The absorption spectrum of potassium vapour at temperatures up to 1300° C. has been studied by Sur and Ghosh (*Phil. Mag.*, **49,** 60, 1925). These workers find that whereas at moderate temperatures the vapour absorbs only the lines $\nu = 1^2S - n^2P_{1,2}$ of the Principal Series of potassium, at much higher temperatures (1200°-1300° C.) a number of the doublets of the first and second Subsidiary Series of potassium appear in the absorption. At 1300° C. the following doublets are observed :—

$$\nu = 2^2P_{1,2} - 4^2S,\ \nu = 2^2P_{1,2} - 5^2S,\ \nu = 2^2P_{1,2} - 6^2S,\ \nu = 2^2P_{1,2} - 7^2D.$$

$$\lambda = \begin{cases} 5802\text{ Å} \\ 5783\text{ Å} \end{cases},\quad \lambda = \begin{cases} 5340\text{ Å} \\ 5323\text{ Å} \end{cases},\quad \lambda = \begin{cases} 5099\text{ Å} \\ 5084\text{ Å} \end{cases},\quad \lambda = \begin{cases} 5112\text{ Å.} \\ 5097\text{ Å.} \end{cases}$$

The excess internal energy of the potassium atom when in the 2^2P_1 or 2^2P_2 state is approximately 1·61 volts (cf. Table XI.) or 37,000 calories per gram-atom. The fraction of the atoms so excited in potassium vapour in thermal equilibrium at 1300° C. is given by $pe^{-37,000/RT}$ where p is the *a priori* probability of the states in question relative to that of the normal unexcited state. In this case $p = 3$, and the fraction of excited atoms is therefore about 2×10^{-5}. This fraction is certainly small, but at the moderately high pressure of potassium vapour presumably obtaining under Sur and Ghosh's experimental conditions, it probably represents an appreciable concentration of atoms in the 2^2P_1 and 2^2P_2 states of excitation.

Reversed lines are of frequent occurrence in emission spectra excited in the electric arc or spark, and are occasionally found even in flame spectra. The reversed line appears as a narrow black band cutting out the centre of the broader emission line. Reversal is due to absorption of this central portion of the emission line by atoms in the cooler zone of metal vapour surrounding the arc or spark, and it indicates the presence in this outer zone of atoms which are in the same initial condition as the end condition of the atoms *in* the arc or spark which emit the line. The ease of reversal of the lines of the Principal Series of the elements of Groups I and II and especially of the Subsidiary Series of the elements of Group III corresponds to the large concentrations of *normal* atoms of these elements which must exist in the outer zones of the arc. Reversal, however, is not confined to lines which contain the basic term, characterising the normal unexcited state, of the element. For many of the elements of Groups I and II, the first lines of the two Subsidiary Series in the arc emission spectrum are also readily reversed through re-absorption by excited atoms in the outer portions of the arc.

We have already mentioned the reversal of certain emission lines of the Balmer series for hydrogen which appear as Fraunhofer lines in the solar spectrum. These lines are absorbed from the continuous background of the sun's emission spectrum by excited hydrogen atoms which are presumably produced and maintained by thermal means in the sun's outer atmosphere. Other instances of reversal due to absorption by excited atoms present in the solar atmosphere are found in the three magnesium Fraunhofer lines at 5184, 5173, and 5167 Å, which correspond to the absorption processes $2^3P_{0,1,2} \rightarrow 2^3S_1$ by magnesium atoms in the $2^3P_{0,1,2}$ states.

King (*Astrophys. J.*, **51**, 13, 1920; **55**, 380, 1922), in his work on the characteristics of absorption spectra produced in the electric furnace, has investigated the absorption of several metal vapours at temperatures between 2000° and 3000° C., and has tested in particular the possibility of obtaining at such temperatures the lines of the Subsidiary Series of the alkali metals in absorption. The metal is volatilised in a tube furnace which is electrically heated and at the middle of which is placed a plug of graphite. This plug serves as a source of illumination for the metal vapour, since it is raised to incandescence by the high temperature and emits a continuous (and practically black body) spectrum which acts as a background for the observation of the absorption lines of the hot metal vapour lying between it and the observation end of the tube. The furnace is so wound that the temperature of the bulk of the absorbing vapour is usually a few hundred degrees below that of the graphite plug. With sodium vapour at 2000° C. or higher, King has observed in absorption the three doublets $\nu = 2^2P_{1,2} - n^2D$ (n = 4, 5, and 6) of the first Subsidiary Series of sodium, and, depending upon the temperature, one or more members of the second Subsidiary Series beginning with $\nu = 2^2P_{1,2} - 3^2S$ (the wave-lengths of the first members of these series lie outside his range of observation). Similar evidence of absorption by atoms thermally excited from the 1^2S to the $2^2P_{1,2}$ states is obtained with potassium, rubidium, and cæsium vapours at temperatures from 2200° to 2300° C.

Absorption by Electrically Excited Atoms.—The passage of an electric discharge through a gas or vapour under reduced pressure causes ionisation, and the emission lines which accompany the discharge characterise the various steps by which the rebinding of an electron to the ionised atom can be effected. As a result of this and also as a result of the numerous collisions between normal atoms and free high-speed electrons in the discharge, there must be present in the gas or vapour not only completely ionised atoms but also neutral atoms in various states of excitation above the normal. If by the passage of the discharge an appreciable stationary concentration of so excited atoms can be maintained, the gas or vapour should under these circumstances give absorption lines not present in its ordinary absorption spectrum and characteristic of the excited atoms as the absorbing units. An example of absorption under such conditions has already been noted in the reversal of the H_α line of the Balmer series of hydrogen which is obtained by longitudinal observation of the discharge in a long Geissler tube containing hydrogen under reduced pressure. Another interesting example is afforded by helium. From the series scheme of the arc spectrum of helium (Fig. 19) it follows that the normal atom can absorb only at wave-lengths below 600 Å and, in fact, helium gas is transparent in the infra-red, visible, and far into the extreme ultra-violet. Paschen (*Ann. Physik*, **45**, 625, 1914) has observed, however, that when a weak electric discharge is passed through helium in a Geissler tube at low pressures, the gas absorbs and fluoresces strongly at the wave-length $1{\cdot}083\,\mu$ and less strongly at $2{\cdot}058\,\mu$ in the near infra-red. These wave-lengths correspond to the transitions $2^3S_1 \rightarrow 2^3P_{1,2}$ and $2^1S_0 \rightarrow 2^1P_1$ (cf. Fig. 19), and their absorption and re-emission by the electrically excited gas clearly indicates the presence in the discharge tube of a considerable fraction of atoms in the metastable 2^3S_1 and 2^1S_0 states. The absorption spectrum in the visible and near ultra-violet of helium under the same conditions has recently been studied by McCurdy (*Nature*, **117**, 122, 1926), who has found further absorption lines originating in the 2^3S_1 and 2^1S_0 energy levels, and also several absorption lines of the series $\nu = 2^3P_1 - \mathrm{n}^3D$ and $\nu = 2^1P_1 - \mathrm{n}^1D$ which point to the presence of appreciable numbers of helium atoms in the still higher states of excitation represented by 2^3P_1 and 2^1P_1. In the same way, neon and argon normally absorb only in the extreme ultra-violet, yet if either gas be subjected at low pressure to a mild electric discharge it absorbs strongly at certain frequencies in the visible (Meissner, *Ann. Physik*, **76,** 124, 1925; *Z. Physik*, **43,** 449, 1927). As a further instance of the phenomenon under consideration, we may also mention the very strong absorption of the lines 5461, 4358, 4047, 3343, and 3663 Å by mercury vapour which is carrying a small electric current (Metcalfe and Venkatesachar, *Proc. Roy. Soc.*, **100**A, 149, 1921). All these lines correspond to transitions in absorption of mercury atoms, already excited to one or other of the 2^3P energy levels, to higher ^3S or ^1D levels (cf. Fig. 18).

In all the examples quoted, the gas or vapour is, of course, ionised by the passage of the electric discharge, and the excited atoms whose absorption lines are noted are formed in the main by recombination of ions and electrons. Ionisation may, however, be avoided and the experimental conditions simplified if the preliminary excitation of the atoms is effected by collisions with electrons of controlled velocity. With this mode of excitation, de Grott (*Naturwiss.*, **14,** 104, 1926) has examined the absorption of excited neon atoms. The neon gas at low pressure is bombarded with a stream of high-speed electrons, the velocities of which are so regulated (accelerating potential between 16 and 18 volts) that only the first states of excitation of the neon atoms, and not complete ionisation, are possible of attainment by collision. When the so excited but non-luminescent gas is now illuminated with the visible radiation of a neon lamp—radiation which ordinary unexcited neon would not, of course, absorb—certain of the neon lines are absorbed and are re-emitted as resonance radiation (fluorescence) in the red and orange. If the accelerating potential of the electron stream falls below 16 volts, the neon atoms are no longer excited by electronic impact, and the optical resonance of the gas for visible light is no longer obtained.

Absorption by Optically Excited Atoms. Consecutive Absorption of Two or More Frequencies by the same Atom.—When the unexcited atom of a monatomic gas or vapour is raised to a higher energy level by the absorption of some line ν_1 of its line absorption spectrum, its usual fate is to revert to the normal state either by re-emission of radiation of the same frequency ν_1 as resonance radiation, or by degradation of its excess internal energy into energy of translatory motion by collision with other atoms. There exists also the possibility, however, if another suitable frequency ν_2 of the line emission spectrum of the element is also present in the illuminating radiation, that the excited atom should go on to absorb this frequency and so be raised to a still higher energy level. The attainment of this would under certain circumstances be indicated by the fluorescent emission of a number of frequencies ν_3, ν_4 . . . of the complete emission spectrum of the element besides the frequencies ν_1 and ν_2 which have actually been absorbed.

An example of such step-by-step excitation of an atom by absorption is found in the behaviour of mercury vapour contained in a quartz (resonance) tube at low pressures and illuminated with the full light of a quartz mercury vapour lamp. The fluorescent emission of the so illuminated vapour was first investigated by Füchtbauer (*Physikal. Z.*, **21,** 635, 1920). The quartz lamp emits all the frequencies of the arc spectrum of mercury, but the quartz is practically opaque to any absorption line of the *normal* mercury atom of wave-length less than 2537 Å. Accordingly, the only state attainable by the illuminated Hg atoms in one elementary act of absorption is the 2^3P_1 state. In spite of this, however, Füchtbauer found in the fluorescent emission from the resonance tube not only the true resonance line 2537 Å of the normal atom, but also a number of lines of the subordinate series of mercury such as the lines 3131 (3^3D_1), 3125 (3^3D_2), 3663 (3^3D_1), 3655 (3^3D_2), 4358 (2^3S_1), and 5461 (2^3S_1), the presence of which could only mean that the higher S and D states of excitation from which these lines originate were attained by the radiating mercury atoms in stages *via* the 2^3P_1 state (cf. Fig. 18). In agreement with this conclusion, Füchtbauer further observed that when the 2537 Å line is filtered out of the incident radiation by interposing a glass plate between the lamp and the resonance tube, all the fluorescent emission from the latter is extinguished.

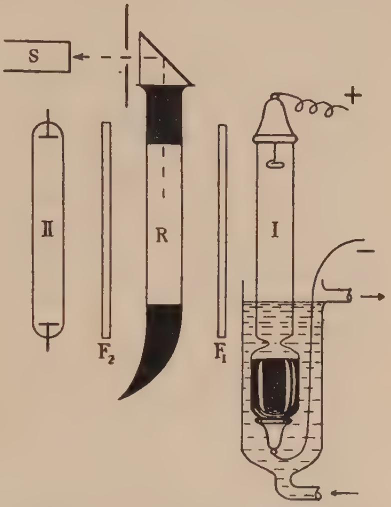

FIG. 24.—Wood's apparatus for activating Hg atoms by the consecutive absorption of two or more frequencies.

Wood (*Proc. Roy. Soc.*, **106** A, 679, 1924; *Phil. Mag.*, **50,** 774, 1925) has refined Füchtbauer's technique by illuminating the mercury vapour in the resonance tube with various combinations of monochromatic frequencies and studying the resultant emission spectra. A diagrammatic representation of Wood's experimental arrangement is shown in Fig. 24. R is the quartz resonance tube, which is thoroughly evacuated and contains only mercury vapour at the very low saturation pressure (about 0·001 mm.) corresponding to room temperature. To the top of this tube is cemented a right-angle quartz prism, which reflects the fluorescent radiation coming from the centre of the tube into the spectroscope S. The tube R is illuminated on the one side by the water-cooled quartz mercury lamp I. This gives a very intense emission of the line 2537 Å, which is necessary always for the first stage of activation of the mercury vapour in R. All the other lines in the emission of lamp I may be cut out by the use of a suitable filter F_1. The resonance tube is also illuminated from the other side by a second mercury vapour lamp II, which, however, is not water-cooled. The resonance line 2537 Å is practically absent in the spectrum of the emission from lamp II, being reversed by self-absorption when the lamp is run hot, but the different lines of the Subsidiary Series of the complete emission spectrum of mercury are strongly in evidence, and a choice can be made of any desired frequency or frequencies which may be required for the second stage of excitation of the mercury atoms in R by suitably filtering the emission from the lamp II. We may detail briefly a few of Wood's results, referring continually to the energy diagram of mercury in Fig. 18. Using for purposes of illumination the water-cooled arc I alone and a bromine vapour filter F_1, the filter transmits no visible light but only the Principal line 2537 Å, and the Subordinate lines 3125, 3131, and 2967 Å in the ultra-violet. No visible fluorescence is excited by this stimulation, but the spectrograph shows the presence of the fluorescent lines 2967, 3125, 3131, 3655, and 3663 Å. The history of the mercury atoms which emit these lines can be traced by Fig. 18 through the stages :—

$$\begin{aligned}&\mathrm{Hg}(1^1S_0) + 2537\ \text{Å} \rightarrow \mathrm{Hg}(2^3P_1)\,;\\ &\mathrm{Hg}(2^3P_1) + 3131 \text{ or } 3125\ \text{Å} \rightarrow \mathrm{Hg}(3^3D_1) \text{ or } \mathrm{Hg}(3^3D_2)\,;\\ &\mathrm{Hg}(3^3D_{1,\,2}) \rightarrow \mathrm{Hg}(2^3P_{0,\,1,\,2}) + 2967\ \text{Å},\ 3125\ \text{Å, etc.}\end{aligned}$$

The second lamp is now lighted. The light from this alone produces no fluorescence of the mercury vapour, since, not being water-cooled, its 2537 Å line is strongly reversed. When used in conjunction with lamp I, however, the ultra-violet 2537 line of lamp I and the violet line 4358 of lamp II are both absorbed and the following consecutive changes are now possible :—

$$\begin{aligned}&\mathrm{Hg}(1^1S_0) + 2537\ \text{Å} \rightarrow \mathrm{Hg}(2^3P_1)\,;\\ &\mathrm{Hg}(2^3P_1) + 4358\ \text{Å} \rightarrow \mathrm{Hg}(2^3S_1)\,;\\ &\mathrm{Hg}(2^3S_1) \rightarrow \mathrm{Hg}(2^3P_{0,\,1,\,2}) + 4047\ \text{Å},\ 4358\ \text{Å, and } 5461\ \text{Å}.\end{aligned}$$

The green fluorescence at 5461 Å is easily recognised under these circumstances.

The relative intensities of emission of the components of the triplet $\nu = 3^3D_{1,\,2,\,3} - 2^3P_2$ in the fluorescence of the mercury vapour under different conditions of excitation are of interest. We may assume that such mercury atoms in the resonance tube as reach the 3^3D states always do so *via* the 2^3P states. Other possible ways of attaining a 3^3D level by step-wise absorption (e.g. $1^1S_0 \rightarrow 2^1P_1 \rightarrow 3^3D_{1,\,2}$), or by absorption followed by emission (e.g. $1^1S_0 \rightarrow 4^3P_1 \rightarrow 3^3D_{1,\,2}$), must be ruled out on account of the relatively very feeble intensity of the required frequencies in the emission of the illuminating lamps. Furthermore, the 3^3D states do not combine with one another in emission or absorption, and although they lie energetically very close to one another and are probably mutually convertible through the agency of collisions, this possibility must also be ruled out on account of the very low pressure in the resonance tube. If now all wave-lengths greater than 4000 Å are cut out of the illuminating radiation by suitable filters, the state 2^3P_1 is attained by the normal mercury atom in a single act of absorption and the line $\nu = 1^1S_0 - 2^3P_1$ constitutes the *primary fluorescence* of the resonance tube. Each of the states 3^3D_1 and 3^3D_2 is reached by two elementary acts of absorption, and as a result we have, among others, the lines $\nu = 2^3P_2 - 3^3D_{1,2}$ (3663 and 3655 Å) present in appreciable intensity as *secondary fluorescence*. The emission of the line $\nu = 2^3P_2 - 3^3D_3$ (3650 Å) may be termed *tertiary fluorescence* since, under the stated conditions, this line can only be emitted subsequent to *three* acts of absorption by the same atom which goes through the sequence of events: $1^1S_0 \rightarrow 2^3P_1 \rightarrow 3^3D_1$ (or 3^3D_2) $\rightarrow 2^3P_2 \rightarrow 3^3D_3$. The relative improbability of occurrence of this sequence explains the vanishingly small intensity of emission under excitation with ultra-violet light of the component $\nu = 2^2P_2 - 3^3D_3$ of the triplet. On the other hand, if the lines 2967, 3131, and 3125 Å be absent from the exciting radiation, but the line 4358 Å present, then of the three lines 3663, 3655, and 3650 Å, the last named is the most intense in the resultant fluorescence. This fact may be explained in the following way. Mercury atoms primarily excited to the 2^3P_1 state can now be further excited only by secondary absorption of the line 4358 Å, which takes them to the 2^3S_1 level. The 3^3D levels can now be reached in a roundabout way by emission of 5461 Å, which takes the atom to the 2^3P_2 level, followed by tertiary absorption of 3663, 3655, or 3650 Å from the incident radiation. Of these three wave-lengths 3650 Å is strongest in the incident radiation, and, for this reason alone, the 3^3D_3 level should be the most frequently attained of the three, consequently the line 3650 Å should be of greater intensity than either 3663 or 3655 Å in the tertiary fluorescence. Added to this is the circumstance that when the mercury atom attains the 3^3D_1 or 3^3D_2 level by absorption of 3663 or 3655 Å from the illuminating radiation, it then has other possibilities of emission besides that corresponding to reversion to the 2^3P_2 state. The existence of these possibilities weakens, of course, the intensity of tertiary fluorescence of the lines 3663 and 3655 Å.

TRANSITION PROBABILITIES.

We have discussed the very large measure of success which attends the application of Bohr's two fundamental postulates to the absorption and emission of radiation by atoms, but it must always be remembered that the description of the quantum processes afforded by these postulates is necessarily of a purely phenomenological character. The first and more fundamental of the postulates discards the classical view of the continuous variability of the physical state of a system, the second prescribes the monochromatic frequencies with which the system in any quantised stationary state is capable of interacting, but tells us nothing regarding the inevitability or otherwise of a certain quantum event which is perhaps possible under the given conditions, that is, we have in the postulates themselves no analogue to the causal laws whereby classical theory describes the elementary physical processes.

In the classical theory of emission and absorption of radiation, the behaviour of a material dipolar oscillator of natural frequency ν in a field of radiation is uniquely determined by a statement of its own parameters and those of the field. On the one hand, if the oscillator possess vibrational energy ϵ, it can radiate this energy spontaneously and continuously at a rate which is independent of the environmental conditions and is governed by the exponential law $-\frac{d\epsilon}{dt} = \alpha\epsilon$. Here α, the damping factor of the oscillation, is a constant characteristic of the oscillator, depending only on its natural frequency of vibration ν and on the universal constants e, m, and c. The reciprocal of α, which has the dimensions of time, is the natural period of decay of the excitation, the time within which the excess energy ϵ falls to $1/e$ of its original value. Apart from this spontaneous emission of energy, the oscillator reacts with the radiation of frequency ν in the surrounding field, and depending upon the phase and amplitude of the waves impinging upon it at any instant, its sympathetic reaction at that instant results either in the abstraction of radiant energy from the field (absorption) or in the transfer of energy to the field (" negative " absorption or induced emission). These also in the classical theory are treated as causal processes; further, they are continuous in nature and capable of description in terms of differential equations relating the microscopic parameters and variables of the field with those of the individual oscillator.

The concept of discontinuity which lies at the basis of the quantum theory makes such a description of emission and absorption out of the question in quantum mechanics. Our lack of certain knowledge as to what determines the actual occurrence of each quantum transition of the material oscillator forces us to replace the causal description of the behaviour of the individual atom or molecule by a vaguer and less satisfactory statement of the statistics of the behaviour of a large number of atoms or molecules under the given conditions. The statistical result is, in the absence of more detailed knowledge, referred back to a set of interconnections between the different stationary states of the individual particle which we call " transition probabilities." To illustrate the nature of these transition probabilities, we may take the case of a large number of similar atoms excited from their normal state to some higher energy level and reverting from this to the normal with emission of monochromatic radiation. Experimentally, it is found (*vide infra*) that the rate of decay of the gross intensity of emission E follows the exponential law $-\frac{dE}{dt} = A \,.\, E$. In terms of the classical theory and the classical oscillator, we should conclude from this result that the continuous decay in the emission of the individual oscillator follows the same law $-\frac{d\epsilon}{dt} = A \,.\, \epsilon$. The quantum interpretation of the same experimental result is very different. Here the falling off in the gross intensity of emission with time cannot be related to a continuous change in the energy of the individual atom during emission. The actual time in which the atom emits a quantum of radiation—the time of transition from one stationary state to another—is to be regarded as extremely small compared with the time during which it remains in the excited state. Accordingly, the amount of energy emitted by the assembly of atoms in a finite time interval simply gives a measure of the number of quantum transitions of atoms from the excited to the normal state which occur during this time interval. Re-writing the experimental observation in the form $-\frac{dN}{dt} = A \,.\, N$, where N denotes the number of excited atoms present in the system at the time t, we see that the number of atoms reverting to the normal state at any instant is simply proportional to the number of atoms capable of such reversion, in other words, the probability of the spontaneous quantum jump is independent of the length of time already spent by the atom in the excited state. This law of spontaneous quantum emission is in all respects similar to the law which governs the disintegration of a radioactive element, and neither process can as yet be treated from the causal standpoint. All that we can infer from the above experimental result is that the measured coefficient A gives the probability that an excited atom should emit its quantum of radiation in unit time. The reciprocal of A is formally the analogue of the natural period of decay of the classical oscillator, and is termed the average life or life period of the atom in the excited state. In speaking of this life period, however, it must be remembered that it is the reciprocal of a probability, and therefore it does not imply any inevitability of occurrence of the event to which it refers.

Einstein's Derivation of the Planck Radiation Law.—The formal nature of the quantum description of the processes of emission and absorption of radiation is exemplified by Einstein's treatment (*Ber. deut. phys. Ges.*, **18**, 318, 1916; *Physikal. Z.*, **18**, 121, 1917) of the temperature equilibrium between a material system comprising a very large number of similar Bohr atoms and a field of radiation. In accordance with Bohr's first postulate, each atom is assumed to be capable of existing only in a discrete series of states $Z_1, Z_2, Z_3 \ldots$ characterised by the energy levels $\epsilon_1, \epsilon_2, \epsilon_3 \ldots$ respectively. Of these states Z_1 may be taken to represent the lowest (normal), $Z_2, Z_3 \ldots$

progressively higher energy levels. By application of the Boltzmann statistical principle, which is of general validity and presumes no special mechanism of energy interchange between atoms and atoms or between atoms and the surrounding field of radiation, it follows that when the system is in thermodynamic equilibrium at the temperature T, the numbers of atoms in the different quantum states $Z_1, Z_2, Z_3 \ldots$ are given by

$$N_1 = a \cdot p_1 \cdot e^{-\epsilon_1/kT};\; N_2 = a \cdot p_2 \cdot e^{-\epsilon_2/kT};\ \text{etc.} \qquad (1)$$

In these equations, a is a factor which depends in general upon the temperature, but is independent of the particular state Z_n considered, and p_n is the statistical weight or *a priori* probability * of the state Z_n.

Einstein now assumes that an atom can pass from the state Z_m to the state Z_n by absorption of monochromatic radiation of frequency ν, and can revert from Z_n to Z_m by emission of radiation of the same frequency. The amount of energy transformed in either process is $(\epsilon_n - \epsilon_m)$. These reciprocal transitions will, in general, be possible for each combination of indices, and each pair of elementary processes must exactly balance one another under the conditions of temperature equilibrium, in other words, just as many atoms must pass per unit time from the state Z_m to the state Z_n by absorption of radiation as pass from Z_n to Z_m by emission. We may confine our attention without loss of generality to the reciprocal processes $Z_m \rightleftharpoons Z_n$, and enquire now into the energy exchanges which take place between the atoms in these states and the temperature radiation of frequency ν which is in equilibrium with them.

In classical theory, the mutual action between an oscillator and radiation involves the three processes of absorption, induced emission, and spontaneous emission. The extent to which the first two occur depends not only on the condition of the oscillator but also upon that of the radiation field, and for a homogeneous field is proportional to the radiant energy density u_ν of the frequency ν with which the oscillator can react. The extent of spontaneous emission depends solely upon the condition of the oscillator itself. For the quantum interaction of atoms and radiation, Einstein assumes the three formally analogous processes :—

(*a*) *Absorption.*—Of the N_m atoms in the state Z_m, a certain fraction pass every second to the state Z_n by absorption of radiation. The number of such transitions per second is proportional to N_m and to the density u_ν of radiation of the absorbed frequency ν in the surrounding field, and is written equal to $B_m{}^n \cdot N_m \cdot u_\nu$. The coefficient $B_m{}^n$ is a constant characteristic of the combination in absorption of the states Z_m and Z_n.

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* The statistical weight or *a priori* probability of any internal energy state of the atom is measured by the total number of ways in which this state can be realised. For each (n, k, j) state of the atom this is given by the number of quantised orientations which the atom can assume under the action of a magnetic field and is $p = 2j + 1$, where j is the *true* inner quantum number of the state.

(*b*) *Induced Emission*.—By sympathetic reaction with the field, atoms in the higher state Z_n are induced to emit. The resulting number of transitions $Z_n \rightarrow Z_m$ per second is given by $B_n{}^m \,.\, N_n \,.\, u_\nu$ where $B_n{}^m$ is another constant characteristic of the combination in emission of the states Z_m and Z_n.

(*c*) *Spontaneous Emission*.—This is expressed by a transition probability $A_n{}^m$, and the number of spontaneous events $Z_n \rightarrow Z_m$ per second is written equal to $N_n \,.\, A_n{}^m$.

At equilibrium, the number of atoms passing by absorption from the state Z_m to the state Z_n must equal the number passing by induced and spontaneous emission from Z_n to Z_m. Hence

$$N_m \,.\, B_m{}^n \,.\, u_\nu = N_n \,(B_n{}^m \,.\, u_\nu + A_n{}^m).$$

Substituting the Boltzmann expressions (1) for N_m and N_n, we obtain

$$p_m \,.\, B_m{}^n \,.\, u_\nu \,.\, e^{(\epsilon_n - \epsilon_m)/kT} = p_n \,.\, B_n{}^m \,.\, u_\nu + p_n \,.\, A_n{}^m$$

or

$$u_\nu = \frac{p_n \,.\, A_n{}^m}{p_m \,.\, B_m{}^n \,.\, e^{(\epsilon_n - \epsilon_m)/kT} - p_n \,.\, B_n{}^m} \quad . \quad . \quad (2)$$

If now we make the natural assumption that u_ν increases without limit as the temperature T increases, it necessarily follows that the denominator becomes zero when $T \rightarrow \infty$, and therefore

$$p_m \,.\, B_m{}^n = p_n \,.\, B_n{}^m \quad . \quad . \quad . \quad . \quad (3)$$

In the special case where $p_m = p_n$, that is, when the inner quantum numbers of the two combining states Z_m and Z_n are the same, this result means that the intrinsic transition probabilities of absorption by the atom Z_m and induced emission by the atom Z_n are equal. Substituting (3) in (2), we obtain

$$u_\nu = \frac{A_n{}^m / B_n{}^m}{e^{(\epsilon_n - \epsilon_m)/kT} - 1} \quad . \quad . \quad . \quad . \quad (4)$$

This, as Einstein points out, is the Planck radiation formula with the constants undetermined. In order to obtain the separate values of the transition probabilities $A_n{}^m$ and $B_n{}^m$ a new electrodynamics, modified in the sense of the quantum principle, is necessary. Without this, however, the ratio of $A_n{}^m$ to $B_n{}^m$ can be deduced. Since u_ν must be a universal function of ν and T, it follows that neither $(\epsilon_n - \epsilon_m)$ nor $A_n{}^m/B_n{}^m$ can depend upon any characteristic of the material model employed other than ν. Further, if equation (4) be compared with the expression for u_ν as given by the functional form of Wien's Displacement Law, viz.

$$u_\nu = \nu^3 \,.\, F\left(\frac{\nu}{T}\right) \quad . \quad . \quad . \quad . \quad (5)$$

it readily follows that

$$\epsilon_n - \epsilon_m \propto \nu \quad . \quad . \quad . \quad . \quad (6)$$

and

$$A_n{}^m/B_n{}^m \propto \nu^3 \quad . \quad . \quad . \quad . \quad (7)$$

The first of these is obviously the Bohr frequency relation $\epsilon_n - \epsilon_m = h\nu$, and the complete form of (7) is obtained by reference to the Planck radiation formula

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1},$$

which requires that

$$A_n{}^m/B_n{}^m = \frac{8\pi h\nu^3}{c^3} \quad . \quad . \quad . \quad . \quad (7')$$

This same result may be obtained more directly and without having recourse to Planck's formula (which, indeed, then follows) if an appeal is made to the fact that the expression (2) for u_ν must reduce in the limit of high temperatures to the Rayleigh-Jeans formula $u_\nu = \frac{8\pi\nu^2}{c^3} \cdot kT$.

AVERAGE LIFE OF AN ATOM IN ANY STATE OF ACTIVATION.

A certain amount of care is necessary in defining what is meant by the average life of an atom in any given state of excitation. Let us first suppose that the activated atom is completely isolated, not only from other material particles, but also from any radiation with which it can react. If the state of excitation is that corresponding to the first energy level above the normal, the only possibility open to the atom is spontaneous reversion to the normal state with emission of radiation. The probability of occurrence of this event is formally expressed by an Einstein coefficient A, and the average life τ of the active state is the reciprocal of this coefficient, $\tau = \frac{1}{A}$ sec. If the state of excitation is higher than the first, there are then in general several possibilities of spontaneous transition. The gross probability of occurrence of these events is $\Sigma A = A_1 + A_2 + A_3 + \ldots$, and the average life of the atom in the excited state in question is $\tau = \frac{1}{\Sigma A}$ sec.

The effective isolation of an atom in the above sense is hardly possible as a practical proposition. Excited atoms are obtained only by thermal collisions with other atoms or molecules, or by inelastic collisions with electrons, or by absorption of radiation, and unless the excited atom can be immediately withdrawn from the environment necessary for its excitation, the possible effects of this environment upon the life of the active state must be considered. When not isolated from other material particles, there exists, of course, the possibility of the atom's deactivation as a result of a collision suffered during its normal life period. The results of a large number of investigations upon the deactivation of atoms and molecules by collision will be dealt with in a later Chapter. At present, we will confine our attention to the behaviour of excited atoms which may be regarded as effectively isolated during their normal life from other atoms or molecules—a condition realised when the monatomic gas or vapour is excited and maintained at a sufficiently low pressure. There remains to be considered the possible effects of radiation upon the life of the active state. Radiation of frequencies which the excited atoms themselves can *absorb* must obviously be excluded, since the absorption of such radiation presents possibilities other than that of spontaneous emission. While this condition is practically realisable, we cannot, of course, exclude radiation of the frequency or frequencies which the excited atoms themselves *emit*. Theoretically, the radiation emitted by one excited atom in reverting to the normal state has a certain capacity to induce other similarly excited atoms in the system to emit also (Einstein's induced emission). It is hardly likely, however, that in a dilute gaseous system the energy density of radiation emitted as a result of excitation is ever sufficient to exert any appreciable effect in this sense. On the other hand, the atoms in a gas or vapour are often activated by intense illumination of the system from without by radiation of the quality which they will subsequently emit, and it is of importance to enquire whether such extraneous illumination can have any perceptible influence on the average life of the excited atoms by inducing them to emission. The ratio of the probability of spontaneous emission to that of induced emission on the part of an excited atom is given by $\frac{A}{B\,.\,u_\nu}$, where A and B are the Einstein emission coefficients as already defined. The ratio A/B is from equation (7′) equal to $\frac{8\pi h\nu^3}{c^3}$. If we assume that the extraneous illumination is derived from black body emission corresponding to a high temperature T, the intensity of illumination of frequency ν is given by $I_\nu = \frac{2\pi h\nu^3}{c^2}\Big/(e^{h\nu/kT} - 1)$. This is equivalent to a radiation density in its path of $u_\nu = \frac{I_\nu}{c}$, where c is the velocity of light. Accordingly, we have

$$\frac{\text{probability of spontaneous emission}}{\text{probability of induced emission}} = \frac{A}{B\,.\,u_\nu} = 4(e^{h\nu/kT} - 1).$$

This quantity is, for the optical range of frequencies and the source temperatures (or intensities of illumination) at our command, very much greater than unity. We may conclude then that the chance of destruction of the activated atom by induced emission is always negligible, and therefore that in the absence of collision effects and of radiation which the active atom itself can absorb, the average life of the active atom is given by $\tau = \frac{1}{A}$, or by $\tau = \frac{1}{\Sigma A}$ when more than one possibility of spontaneous emission is available.

Evaluation of "τ" from Principle of Correspondence.—From the theoretical standpoint, an approximate estimate of the magnitude of τ is suggested by the Principle of Correspondence. On the basis of the general thesis that the observed effects of essentially quantum phenomena must conform to the predictions of classical theory in the limit of small frequencies or large quantum numbers, Stern and Volmer (*Physikal. Z.*, **20,** 183, 1919) have shown that the probability of spontaneous emission of a Planck oscillator in its first state of excitation ($\epsilon = h\nu$) should be approximately equal to the classical damping factor of the vibration as defined by the exponential law of decay $-\frac{d\epsilon}{dt} = \alpha \,.\, \epsilon$. It follows that the average life of the oscillator in its first quantum state of excitation is roughly equal to the natural period of decay of the same oscillator when treated according to the classical laws. This natural period of decay is given by

$$\tau_{(\text{classical})} = \frac{3mc^3}{8\pi^2 e^2 \nu^2}.$$

For frequencies of vibration of the oscillator corresponding to the optical range $\nu = 4 - 8 \times 10^{14}$ sec.$^{-1}$, the value of $\tau_{(\text{classical})}$ is about 10^{-8} sec., and the value of $\tau_{(\text{quantum})}$ for the oscillator should be at least of this same order of magnitude. For the material atom the motion of its optical electron is, of course, more complex than that of the electron in the simple Planck oscillator, but this motion can always be analysed into a Fourier series of vibrations which represent successive harmonics of a fundamental frequency. The quantum combination in emission of any two states of excitation of the atom then " corresponds " to the simultaneous occurrence of a certain harmonic in the Fourier series for the two combining states. This harmonic of the motion in either state has a classical damping factor, and the probability of the spontaneous quantum transition correponds with this in order of magnitude. It follows from this that the average life of the lowest *labile* states of excitation of an atom should also be approximately 10^{-8} sec. We stress the fact that the state of excitation here considered should be a labile state, since the atom has theoretically an infinite life in any *metastable* state of excitation in the absence of disturbing effects such as collisions or strong electric or magnetic fields. The Selection Principles which forbid the combination in emission of a metastable state with any lower state of the atom are an expression of the fact that the quantum transition involved has no counterpart in the classical picture, that is, there is no Fourier harmonic in the motion of the system in one or other of the two quantised states considered which corresponds to the required change in quantum numbers.

Wien's Method of Measuring "τ".—The order of magnitude of the life of the labile active state which is predicted by the Correspondence Principle has been amply verified within recent years. Probably the most favourable conditions for measuring τ experimentally are those realised by Wien by the following simple arrangement. A canal ray tube—a discharge tube divided into two compartments by the cathode which is perforated by a long narrow capillary orifice—is employed. A steady and fairly low pressure of, say, hydrogen is maintained in the discharge chamber against the slow leak through this orifice into the observation chamber which is kept highly evacuated by the continuous operation of mercury vapour pumps, liquid air traps, etc. The molecular hydrogen in the discharge tube is dissociated and the atoms ionised by a powerful electric discharge. The $+^{ve}$ hydrogen ions are powerfully accelerated towards the cathode by the field, and a small fraction of those which reach the cathode pass through the orifice in this and penetrate with very high velocities into the observation chamber. It is not these charged canal rays themselves in which we are interested, but the excited neutral hydrogen atoms, formed near the cathode by recombination of high-speed ions with electrons, which retain the very high velocity of the ions from which they were formed, and, passing through the cathode orifice, give a unidirectional jet of luminescing atoms which may stretch for several centimetres into the observation chamber. In the visible luminescence of this stream of canal rays, the lines H_α, H_β, and H_γ of the Balmer series are most prominent, corresponding to transitions of excited hydrogen atoms from higher states to the $n = 2$ state of excitation. The pressure of residual gas in the observation chamber being maintained as low as possible, collision effects are excluded, and the only fate open to any excited atom in the stream is reversion to a lower state of excitation by spontaneous emission. Since this reversion is governed by probability laws, the intensity of any line in the luminescence of the jet when transversely observed should then be greatest at the point of entry, and should fall off logarithmically with increasing distance of penetration of the excited atoms into the observation chamber. If the common velocity of the excited atoms in the stream is v, the intensity of any line should decrease proportionately to $e^{-Ax/v}$, where A is the Einstein transition probability for the emission process, and x is the distance of penetration from any chosen origin. Wien's observations with hydrogen in the discharge tube are in general agreement with this predicted behaviour, and the values of A which he computes from his observations are of the expected order of magnitude. For the evaluation of A from measurements of the rate of decay of the luminosity with distance of penetration, the value of the velocity v of the atom stream is required. This is obtained by observation of the magnitude of the Doppler shift $\delta\lambda$ in the wave-length of the emitted radiation and substitution in the relation $v = \frac{\delta\lambda}{\lambda} \cdot c$.

Table XIII. contains a summary of values of A for different quantum transitions as measured by Wien (*Ann. Physik*, **73,** 483, 1924; **83,** 1, 1927) and by Kerschbaum (*ibid.*, **79,** 465, 1926; **83,** 287, 1927) by this method.

TABLE XIII.

TRANSITION PROBABILITIES MEASURED BY WIEN'S METHOD.

Element.	Spectral Lines.	$A \times 10^{-7}$ (sec.$^{-1}$).
H (arc)	Balmer lines H_α, H_β, H_γ Lyman lines H_a, H_b	5·40 14·8
He (arc)	$\nu = 2^3P_2 - 4^3D_3$ (λ = 4472 Å)	5·42
Hg (arc)	$\nu = 2^3P_1 - 2^3S_1$(λ = 4358 Å) $\nu = 1^1S_0 - 2^3P_1$(λ = 2537 Å)	5·50 1·02
Li (arc)	Principal and 1st Subordinate lines λ = 6708, 6103, 4603, and 4132 Å	1·54
Na (arc)	$\nu = 1S - 2P_{1,2}$(λ = 5890/6 Å) $\nu = 2P_{1,2} - 7D$(λ = 4494/8 Å)	2·7
Ca (arc)	$\nu = 1^1S - 2^1P$(λ = 4227 Å)	2·8
Ca (spark)	λ = 3933 and 3968 Å	15·4
Sr (arc)	$\nu = 1^1S - 2^1P$(λ = 4607 Å)	5·05
Sr (spark)	λ = 4305 Å λ = 4077, 4215, 4165 Å	2·78 8
Ba (spark)	λ = 4554 Å λ = 4934, 4130, 4900, 4525 Å	3·7 8·3
O_2 (arc)	λ = 6158 and 4368 Å	0·67
O_2 (spark)	λ = 467, 459, 441, 435, 419 $\mu\mu$	6·54
N_2 (arc)	λ = 6610, 4113, 4105 Å	1·06
N_2 (spark)	λ = 533, 500, 443, 399 $\mu\mu$	7·40

One interesting result of these measurements, the theoretical significance of which is as yet obscure, is that the probabilities of the spontaneous transitions which give rise to different lines in the spectrum of an element are in many cases equal within the limits of experimental accuracy. Several examples of this are to be found in the table. In particular we may note that for the lines H_α, H_β, and H_γ of the Balmer series of hydrogen, the A's of the interorbital transitions $n = 3 \rightarrow n = 2$, $n = 4 \rightarrow n = 2$, and $n = 5 \rightarrow n = 2$ are all equal to $5{\cdot}4 \times 10^7$ sec.$^{-1}$, while for the lines H_a and H_b of the Lyman series, the A's of the interorbital transitions $n = 2 \rightarrow n = 1$ and $n = 3$

$\rightarrow n = 1$ are both equal to $14{\cdot}8 \times 10^{7}$ sec.$^{-1}$. Again, while the values of the A's agree in general as regards order of magnitude with the corresponding classical damping factors, it must be remarked that the wave-length of the radiation emitted, which determines the value of the classical damping factor of an oscillator emitting such radiation, plays a decidedly minor rôle in the value of the quantum transition probability. The wave-length of the line H_α is 5·4 times that of H_a, and the classical damping factor should therefore be 29·4 times less, whereas the quantum transition probability is only 2·74 times less.

The average life of an atom in any state of excitation can be calculated only if the probabilities of all the available spontaneous transitions from this state are known. For the state $n = 2$ of the hydrogen atom there is but one possibility of spontaneous emission, corresponding to the line H_a of the Lyman series. The average life of the hydrogen atom in the state $n = 2$ is therefore $\tau = \frac{1}{A} = 6{\cdot}76 \times 10^{-9}$ sec. For the state $n = 3$ of the same atom there are two possibilities of spontaneous emission, $3 \rightarrow 1$ and $3 \rightarrow 2$, which give rise to the lines H_b of the Lyman series and H_α of the Balmer series respectively. The average life of the atom in this state is then $\tau = \frac{1}{\Sigma A} = \frac{10^{-7}}{5{\cdot}4 + 14{\cdot}8} = 5 \times 10^{-9}$ sec. Again, the average life of the mercury atom in the 2^3P_1 state is simply the reciprocal of the transition probability corresponding to $2^3P_1 \rightarrow 1^1S_0$, viz., $\tau = 9{\cdot}8 \times 10^{-8}$ sec., but the average life of the atom in the 2^3S_1 state is not the reciprocal of $A = 5{\cdot}50 \times 10^{7}$ sec.$^{-1}$, since, besides the transition $2^3S_1 \rightarrow 2^3P_1$ which this characterises, there are other possibilities of transition, viz., $2^3S_1 \rightarrow 2^3P_{0,2}$ and $2^3S_1 \rightarrow 2^1P_1$, the A's of which are unknown.

Other Methods of Estimating "τ."—The success of Wien's method of measuring A or τ depends upon the fact that the excited atoms enter the observation chamber with very high velocities (10^7 — 10^8 cm./sec.) which are just of the right order to spread the luminescence due to reversal over an appreciable distance. Previous to Wien's measurements, attempts had been made to determine the average lives of excited atoms or molecules, formed by absorption of radiation, by a comparison of the spectral limits of the zone of illumination of a unidirectional jet of a gas or vapour with those of the zone of re-emission of the absorbed radiation as fluorescence. The idea underlying such investigations is, of course, that a fraction of the atoms or molecules which are excited by absorption when just within the zone of illumination should be carried beyond this zone, by virtue of their translatory motion, before they re-emit. Dunoyer (*Compt. rend.*, **156,** 1007, 1913) shone a sharply defined pencil of sodium D light transversely upon a unidirectional stream of sodium atoms, but was unable to detect any displacement of the position of resonance relative to that of illumination. Wood (*Phil. Mag.*, **24,** 673, 1912) obtained a similar negative result, using a stream of iodine vapour illuminated with sunlight (which induces iodine to fluorescence).

If we accept Kerschbaum's value of A for the transition $2P_{1,2} \rightarrow 1S$ for sodium, the average life of the excited sodium atom is about 3.10^{-8} sec. Accordingly, Dunoyer's negative result simply means that his stream velocity—*circa* 10^5 cm./sec.—was much too small to produce any appreciable shift of the excited atoms within their lifetime. That Wood's negative result with iodine was also due to insufficient stream velocity, and not to destruction of excited molecules outside the zone of excitation by molecular collisions, was shown by Stern and Volmer (*Physikal. Z.*, **20,** 183, 1919). Iodine vapour at a pressure of 0·2 mm. Hg was illuminated with a narrow pencil of sunlight, and the cross-sectional limits of the fluorescent zone accurately noted by observation transversely to the path of the exciting beam. The mean free path of the iodine molecules at this pressure is 0·09 mm. Other conditions remaining the same, the pressure was now lowered to 0·03 mm., whereby the mean free path of the iodine molecules is raised to 0·6 mm. In spite of this, the cross-sectional limits of the fluorescent emission remained as before. Stern and Volmer calculate, however, that with an average life of the excited iodine molecules of 10^{-6} sec., a sensible shift in the limits of the fluorescent beam should have been observed. The absence of any such shift therefore gives 10^{-6} sec. as an *upper* limit for the average life of these excited molecules.

Wood has observed that when mercury vapour is illuminated with light of wave-length 2536·7 Å, the vapour emits resonance radiation not only within, but also in a narrow region outside, the spatial limits of the incident beam itself. The average velocity of the mercury atoms at the working temperature is only $1{\cdot}7 \times 10^4$ cm. per sec., and this, taken in conjunction with the observed extent of "diffusion" of the resonance outside its proper limits, indicates an average life of the 2^3P_1 state of at least 10^{-5} sec. The great discrepancy between this value of τ and the value 10^{-7} sec. resulting from other observations suggests, however, that the resonance radiation observed by Wood outside the zone of illumination cannot possibly be emitted by Hg atoms which were activated within this zone and subsequently travelled outside it. Rather, this radiation must be of a secondary character and due to excitation of atoms already outside the zone of primary illumination by the resonance emission from this region. Such an explanation is supported by the very powerful absorptive capacity of mercury vapour at low pressures for its own resonance radiation.

A more successful method for determining the duration of luminescence of an atom which has been excited by the absorption of radiation depends upon the observation of the extent of polarisation of the resonance radiation which it emits when subjected to the influence of a weak magnetic field. If mercury vapour at very low pressures is induced to resonance in the absence of a magnetic field by illumination with plane polarised radiation of wave-length 2536·7 Å, the resonance emission when viewed in a direction perpendicular to that of the incident beam is found to be almost completely polarised. When, however, the mercury vapour is subjected to the influence of a weak magnetic field, the resonance emission produced by illumination with polarised light is only partially polarised. The depolarising action of the magnetic field is strongest when the lines of magnetic force run perpendicular to the electric vector of the incident radiation, and it increases progressively with increasing strength of the field. For the mercury resonance, a field of about 2 Gauss is sufficient to depolarise completely the resonance radiation; for the sodium D resonance, however, a field strength of at least 100 Gauss is necessary.

The theory of this effect of a magnetic field upon resonance radiation need not detain us. We are here interested only in the prediction of the theory that the extent of depolarisation should be related to the average life of the resonating atoms in the excited state by the equation

$$\frac{p}{p_0} = \frac{1}{\sqrt{1 + 4a\tau^2H^2}}.$$

Here H is the strength of the field, p and p_0 are the degrees of polarisation of the resonance radiation with and without the field respectively, a is a constant which can be calculated from the Zeeman resolution of the resonance line, and τ is the average life of the atoms when excited by absorption. The predicted dependence of p upon H has been experimentally verified in a few cases (cf. Kreusler, *Physikal. Z.*, **27,** 313, 1926; Ellett, *J. Opt. Soc. Amer.*, **10,** 427, 1925), and values of τ have been computed from the observations. For the mercury atom in the 2^3P_1 state the value of τ is found to be $1{\cdot}1 \times 10^{-7}$ sec. in excellent agreement with Wien's result (cf. Table XIII.). For the sodium atom in the 2^2P_2 state, reversion from which gives the D_2 line, the computed value of τ is 1×10^{-8} sec., which also agrees reasonably well with Kerschbaum's figure obtained by Wien's method.

WIDTH OF SPECTRAL LINES.

An indirect method of estimating the probability of spontaneous emission on the part of an excited atom or molecule depends upon the fact that the three Einstein coefficients $A_n{}^m$, $B_n{}^m$, and $B_m{}^n$ which symbolise the possibilities of occurrence of the reversible processes $Z_n \rightleftharpoons Z_m$ by spontaneous emission, induced emission, and absorption respectively are related to one another in a simple manner by equations (3) and (7′). Knowing any one of these quantities, the other two can easily be calculated. Since the absorption factor $B_m{}^n$ must be connected in some way with the ordinary absorption coefficient of the gas or vapour for the radiation which can effect the transition $Z_m \rightarrow Z_n$, it follows that the probability $A_n{}^m$ of the spontaneous reversal $Z_n \rightarrow Z_m$ should be possible of derivation from absorption measurements.

Before deriving the relation between the Einstein factor $B_m{}^n$ and the measured coefficient of absorption to which it corresponds, we must first discuss briefly what we really mean by an optical absorption or emission "line." The lines in the emission or in the absorption spectrum of a substance may be obtained very sharp and narrow under properly chosen conditions, but each individual line is always found to possess a finite width in the wave-length or frequency scale. What we call the wave-length of the observed line is actually that of the position of maximum intensity within an indefinite region of emission or absorption. On either side of this point the intensity falls off continuously but extremely rapidly, and the width of the line is defined as the wave-length or frequency difference between the points on either side of the maximum at which the intensity has fallen to half the peak value. The experimentally observed width of a spectral line is not an intrinsic property of the line itself but depends upon the conditions under which the material system absorbs or emits it. In general, the line broadens more or less symmetrically both with increasing pressure at constant temperature and with increasing temperature at constant pressure. A weak electric or magnetic field acting upon the material system also has a broadening effect upon the line, which develops into a Stark or Zeeman resolution of the line for sufficiently strong fields. Each Stark or Zeeman component of the original line is, however, affected by pressure and temperature in the same way as is the unresolved line in the absence of the field.

Natural Width.—In discussing the finite width of an observed spectral line, the first question which arises is whether the line can ever be really monochromatic or whether it must always have an ultimate natural width beyond which it cannot be further narrowed. We must here differentiate between the possibility of emission of a strictly monochromatic frequency and the possibility of observing it as such. Even if the monochromatic emission were possible on the part of an isolated atom or molecule, any practical means of observing it by spectroscopic apparatus would show the emission as a line of finite breadth with an internal distribution of intensity which would be characteristic of the measuring apparatus employed. Passing over this difficulty of possible observation, the first view amounts to accepting Bohr's two postulates in their strictest sense, an acceptance which hardly appears to be justifiable when we consider on the one hand the purely formal nature of the quantum postulates, and on the other our complete ignorance of the dynamics of the atom in the interval of transit between two stationary states. A definite natural width to a spectral line is suggested by the fact that there exists an inherent lack of sharpness in our description of the quantised stationary states of the atoms, a lack of sharpness which is due to the neglect of the atom's reaction with radiation in the equations of motion which constitute one criterion for the mechanical stability of the system. Again, in the classical theory of the emission of radiation by a simple harmonic oscillator of natural frequency ν, the isolated oscillator does not emit a strictly monochromatic radiation. There is a "radiation damping," due to the finite time taken to radiate a finite amount of energy, and as a result the actual emission consists of a narrow range of frequencies about the value ν. The natural half-width of the classical emission line is equal in the frequency scale to the reciprocal of the natural period of decay of the oscillator, and for optical frequencies is of the order of magnitude 10^{-4} Å. A finite duration of the quantum process of radiation would appear to require a corresponding natural width for the line emitted in the quantum transition. We cannot, however, affix any definite value to the duration of the quantum process of emission itself, since, although we may know the average life of the atom in any quantum state of excitation, we do not know what controls the actual emission of the individual, or even how its average life in the excited state is divided between existence in that state and transition to the lower state. Minkowski (*Z. Physik*, **36,** 839, 1926) has attempted to deduce the natural width of the sodium D lines on the basis of the following considerations. From the classical theory of dispersion and absorption, it appears that even when the actual width of an absorption line due to Doppler effect is great compared with the natural width due to radiation damping, the absorption coefficient within the line but sufficiently far from the centre should be independent of Doppler effect. Accordingly, it should be possible to estimate the natural width of the absorption line from measurements (carried out at sufficiently low pressures so that pressure broadening is avoided) of the distribution of intensity within the line broadened by Doppler effect. From such measurements, Minkowski calculates that the natural half-width of the D_1 or D_2 line in absorption is $0{\cdot}62 \times 10^8$ sec.$^{-1}$ in the frequency scale or 7×10^{-4} Å in the wave-length scale. If this value, which agrees reasonably well with the classical estimate, is anything like a true measure of the natural width of such a line, we may conclude that for all practical purposes the natural width of the line may be ignored compared with the artificial broadening always present and due to Doppler effect and pressure broadening.

Doppler and Pressure Broadening.—In classical theory the observed frequency of the radiation which an isolated oscillator of natural frequency ν emits depends upon the translatory velocity of the oscillator relative to the observer. If the oscillator is moving with a velocity v in a direction making an angle θ with the line which connects it with the observer, the frequency of the observed emission is given by

$$\nu_{\text{obs.}} = \nu\left(1 + \frac{v}{c}\cos\theta\right).$$

Similarly, if the oscillator is absorbing radiation from a directed beam, the frequency absorbed depends in the same way upon the velocity of the oscillator relative to the source of the radiation. For a system comprising a large number of oscillators moving in all directions with Maxwellian distribution of their translatory velocities, this Doppler effect results in a symmetrical broadening of the line absorbed or emitted about the central value ν, and the Doppler half-width of the line is given by

$$\Delta\lambda = 3{\cdot}58 \times 10^{-7} . \lambda . \sqrt{\frac{T}{M}},$$

where T is the absolute temperature of the system and M is the " molecular weight " of the oscillators. A Doppler effect of exactly the same magnitude can be accounted for, as Schrödinger has shown, on the basis of the extreme light quantum hypothesis. The actual existence of the effect is, of course, amply evidenced in the changes found in the wave-lengths of the characteristic lines of the elements in the spectra of stars, also in the diffuseness of the emission lines obtained from high temperature sources. For low temperature emission lines the effect is inconsiderable, and may be altogether eclipsed by the broadening due to pressure or to subsidiary effects of the exciting electrical field. Again, under the conditions of most absorption measurements, the Doppler broadening of an absorption line is masked by the more pronounced broadening due to pressure (pressure broadening of the D lines of sodium in absorption becomes noticeable at a pressure of sodium vapour of about 0·01 mm. Hg). This effect owes its origin to the circumstance that every quantum level of an atom or molecule can be modified to a variable degree by the proximity of other atoms and molecules—probably an effect of the stray fields of neighbouring atoms or molecules. As a result, absorption lines broaden, not only with increasing partial pressure of the absorbing substance itself, but also with increasing partial pressure of any diluent non-absorbing gas present. As a general rule, however, addition of a diluent gas is not nearly so effective in broadening an absorption line as is an increase in the partial pressure of the absorbing substance itself. Thus sodium vapour is between ten and twenty times more effective than hydrogen in broadening the D lines in absorption.

The intensity of absorption of any frequency within the narrow region of continuous absorption which constitutes a " line " is generally considered to be a measure of the fraction of molecules or atoms which are in such a condition (of translatory motion and environment) that they can absorb that frequency. This presumption is only justifiable, however, if the intrinsic probability $B_m{}^n$ of transition of the atom or molecule by absorption from the general energy level Z_m to the general energy level Z_n is independent of the slight variability in the states Z_m and Z_n which gives the line its finite width. That $B_m{}^n$ is not a constant within the absorption line seems to be indicated by the results of some experiments of Füchtbauer, Joos, and Dinkelacker (*Ann. Physik*, **71,** 204, 1923). These authors found that the *total* intensity of absorption of mercury vapour at a given vapour pressure for radiation corresponding to the transition $1^1S_0 \rightarrow 2^3P_1$ ($\lambda = 2537$ Å) drops by about 50 per cent. when nitrogen at a pressure of 50 atmospheres is added to the vapour. The presence of the nitrogen, of course, broadens the region of absorption and lowers the fraction of atoms which are capable of absorbing any particular frequency within the line, but if $B_m{}^n$ throughout the broadened line had the same value as in the narrow absorption line of the pure vapour itself, the total intensity of absorption should not have been affected. It should be pointed out, however, that the conclusion that $B_m{}^n$ varies throughout the line is not inevitable. The conditions are extreme, and it is possible that, in the presence of the nitrogen, every mercury atom in the system is no longer capable of the transition $1^1S_0 \rightarrow 2^3P_1$. On general considerations, it seems probable that there is no large variation of $B_m{}^n$ in passing across a moderately narrow absorption line, and, in the theoretical considerations which follow, the Einstein coefficients will be regarded as constants for all points within the spectral line. We now proceed to examine how the Einstein transition coefficients may be calculated from absorption measurements upon the pertinent spectral lines.

RELATION BETWEEN THE EINSTEIN "ABSORPTION" COEFFICIENT $B_m{}^n$ AND THE OPTICAL COEFFICIENT OF ABSORPTION.*

Consider a beam of continuous radiation of total intensity I (ergs per square cm. per second) falling on a layer of the absorbing gas or vapour of thickness dx. The incident energy which is contained within any narrow frequency range between ν and $\nu + \delta\nu$ is given by $I_\nu \, . \, \delta\nu$, where I_ν is defined by $I_\nu = \frac{\partial I}{\partial \nu}$ and is termed the intensity of the illuminating radiation for the frequency ν. Since the radiation travels with velocity c, the radiation density u_ν of the frequency ν resulting from the directed beam is given by

$$u_\nu = \frac{I_\nu}{c} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We require the diminution of I_ν at all points within the absorption "line" ν, which corresponds to the transition $Z_m \rightarrow Z_n$, due to absorption by the layer dx of gas.

If N_m is the total number of atoms of the absorbing substance per cubic centimetre in the state Z_m, the number of such atoms in the layer of unit cross-section and thickness dx is $N_m \, . \, dx$. The number of these atoms which, by virtue of their translatory motion and the effects of the fields of neighbouring atoms or molecules, are capable of absorbing within the narrow frequency interval between ν and $\nu + \delta\nu$ is given by

$$\frac{\partial N_m}{\partial \nu} \, . \, \delta\nu \, . \, dx.$$

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* Cf. Füchtbauer, *Physikal. Z.*, **21**, 322, 1920; Tolman, *Phys. Rev.*, **23**, 699, 1924. The present derivation is practically that given by Tolman in *Statistical Mechanics with Applications to Physics and Chemistry* (A.C.S. Monograph, Chem. Cat. Co., 1927).

Each of these atoms has a specific probability $B_m{}^n$ of absorbing a quantum $h\nu$ of radiant energy from a field of radiation for which u_ν is unity. Hence the actual rate at which energy in the narrow frequency range between ν and $\nu + \delta\nu$ is being removed from the beam is given by

$$h\nu\left(\frac{\partial N_m}{\partial \nu} \,.\, \delta\nu \,.\, dx\right) . B_m{}^n \,.\, u_\nu.$$

On the other hand, by induced emission, radiation coherent with the incident beam is returned to it at the rate

$$h\nu\left(\frac{\partial N_n}{\partial \nu} \,.\, \delta\nu \,.\, dx\right) . B_n{}^m \,.\, u_\nu.$$

The difference of these two rates gives the net decrease in the radiant energy passing per second through the layer. Substituting for u_ν from equation (8), we then obtain

$$-\,d(I_\nu \,.\, \delta\nu) = \frac{h\nu}{c} \,.\, I_\nu\left(\frac{\partial N_m}{\partial \nu} \,.\, B_m{}^n - \frac{\partial N_n}{\partial \nu} \,.\, B_n{}^m\right)\delta\nu \,.\, dx$$

or
$$-\,\frac{1}{I_\nu} \,.\, \frac{dI_\nu}{dx} = \frac{h\nu}{c}\left(\frac{\partial N_m}{\partial \nu} \,.\, B_m{}^n - \frac{\partial N_n}{\partial \nu} \,.\, B_n{}^m\right).$$

However, the left-hand side of this equation is equal to the optical absorption coefficient α_ν of the absorbing medium for light of the frequency ν, since this coefficient is defined by the relation

$$(I_\nu)_{x=x} = (I_\nu)_{x=0} \,.\, e^{-\alpha_\nu \,.\, x}.$$

Accordingly, we have

$$\alpha_\nu = \frac{h\nu}{c}\left(\frac{\partial N_m}{\partial \nu} \,.\, B_m{}^n - \frac{\partial N_n}{\partial \nu} \,.\, B_n{}^m\right).$$

If now we plot the measured values of α_ν at various points within the absorption line as a function of ν and integrate under the curve across the whole width of the line, we obtain

$$\oint \alpha_\nu \,.\, d\nu = \oint \frac{h\nu}{c}\left(\frac{\partial N_m}{\partial \nu} \,.\, B_m{}^n - \frac{\partial N_n}{\partial \nu} \,.\, B_n{}^m\right) . \,d\nu.$$

Since in most cases ν varies but slightly in crossing the effective width of the line, and since, as already stated, we may regard the coefficients $B_m{}^n$ and $B_n{}^m$ as constants within the line, the right-hand side of this equation may be integrated to give

$$\oint \alpha_\nu \,.\, d\nu = \frac{h\nu}{c}\{B_m{}^n \,.\, N_m - B_n{}^m \,.\, N_n\} \qquad . \qquad . \quad (9)$$

To simplify this equation further, we make use of the fact that when the difference in the energy levels Z_m and Z_n corresponds to the absorption of a frequency even as low as in the near infra-red, the intensity of illumination used in absorption measurements is not nearly sufficient to produce a stationary concentration of atoms in the state Z_n which is at all comparable with the concentration of atoms in the lower state Z_m. Hence $N_n \ll N_m$, and since the B's are of the same order of magnitude, equation (9) reduces to

$$\oint \alpha_\nu \,.\, d\nu = \frac{h\nu}{c} \,.\, B_m{}^n \,.\, N_m$$

or

$$B_m{}^n = \frac{c}{h\nu \,.\, N_m} \,.\, \oint \alpha_\nu \,.\, d\nu \quad . \quad . \quad . \qquad (10)$$

Before proceeding, we may emphasise the conditions which have been assumed in deriving this relation:—

(*a*) The width of the absorption line must be sufficiently small to permit of ν being taken as a constant within it.
(*b*) The Einstein B's are regarded as constants within the line.
(*c*) The temperature of the absorbing system is assumed to be sufficiently low, the intensity of illumination sufficiently low, and the frequency of the absorbed radiation sufficiently high so that N_n can be neglected compared with N_m.

We may take it that all these conditions are fulfilled as approximately as is necessary in the optical absorption lines of gases and vapours at moderate temperatures and fairly low pressures.

The Average Life of an Excited Atom or Molecule as Derived from Absorption Measurements.—From the value of the Einstein coefficient $B_m{}^n$ as given by equation (10), we can now infer the value of the probability coefficient $A_n{}^m$ of spontaneous reversion of the atom or molecule from the state Z_n to Z_m. Remembering that

$$A_n{}^m / B_n{}^m = \frac{8\pi h\nu^3}{c^3}$$

and

$$p_n \,.\, B_n{}^m = p_m \,.\, B_m{}^n,$$

it immediately follows that

$$A_n{}^m = \frac{8\pi\nu^2}{c^2} \,.\, \frac{1}{N_m} \,.\, \frac{p_m}{p_n} \,.\, \oint \alpha_\nu \,.\, d\nu \quad . \quad . \qquad (11)$$

The reciprocal of $A_n{}^m$ is the average life τ of the atom or molecule in the excited state Z_n, provided that reversion to the state Z_m by spontaneous emission is the only change which can occur.

As an example of the application of the foregoing considerations, we may take Füchtbauer, Joos, and Dinkelacker's calculation (*loc. cit.*) of the value of the intrinsic probability of absorption of the 2537 Å line by mercury vapour, and Tolman's deduction from this of the average life of the labile 2^3P_1 state of the mercury atom. Füchtbauer, Joos, and Dinkelacker carried out measurements of the absorption coefficient α_ν of mercury vapour (for a definite temperature and saturated vapour pressure) at a series of positions within the absorption line 2537 Å. To facilitate measurement the line was artificially broadened in absorption by addition of a diluent gas such as hydrogen, argon, or carbon dioxide at various pressures. For a definite pressure of a given diluent gas, the absorption curve was obtained by plotting the measured α_ν against ν, and graphical integration under this curve gave the value of $\oint \alpha_\nu \, . \, d\nu$. The value of $\oint \alpha_\nu \, . \, d\nu$ corresponding to zero pressure of the diluent gas was then obtained by extrapolation. The value of N_m of equation (10) for the present case is simply the total number of atoms of mercury per cubic centimetre, and can be calculated from the known vapour pressure of the mercury.

All the data are then available for calculating $B_m{}^n$ which works out to $2{\cdot}88 \times 10^{18}$ in c.g.s. units. To evaluate $A_n{}^m$ we further require to know the ratio p_m/p_n of the *a priori* probabilities of the 1^1S_0 and 2^3P_1 states of the mercury atom. Since $p = 2j + 1$, this ratio is 1 : 3, and the probability of spontaneous reversion of the mercury atom from the 2^3P_1 to the 1^1S_0 state becomes $9{\cdot}68 \times 10^6$ sec.$^{-1}$. From this, the mean life τ of the mercury atom in the labile 2^3P_1 state works out to $1{\cdot}03 \times 10^{-7}$ sec., a value which is in remarkably good agreement with the values $0{\cdot}98 \times 10^{-7}$ and $1{\cdot}1 \times 10^{-7}$ sec. obtained from Wien's method and from the depolarisation of the mercury resonance radiation respectively.

In the following table are given the results of Tolman's calculations for mercury, sodium, and cæsium, based on the absorption measurements of Füchtbauer and co-workers. The values of the ratio p_m/p_n originally used by Tolman have been corrected in conformity with more recent views on the *a priori* probabilities of quantum states, and the A's and τ's have been correspondingly corrected.

TABLE XIV.

Transition Probabilities from Absorption Measurements.

	Line.	λ	$B_m{}^n$	p_m/p_n	$A_n{}^m$	τ
Hg .	$1^1S_0 - 2^3P_1$	2537 Å	$2{\cdot}88 . 10^{18}$	1/3	$9{\cdot}68 . 10^6$	$1{\cdot}03 . 10^{-7}$
Na .	$1^2S_1 - 2^2P_2$	5890	$2{\cdot}32 . 10^{19}$	1/2	$9{\cdot}31 . 10^6$	$1{\cdot}07 . 10^{-7}$
	$1^2S_1 - 2^2P_1$	5896	$1{\cdot}22 . 10^{19}$	1/1	$9{\cdot}75 . 10^6$	$1{\cdot}03 . 10^{-7}$
Cs .	$1^2S_1 - 3^2P_2$	4555	$2{\cdot}00 . 10^{18}$	1/2	$1{\cdot}74 . 10^6$	$5{\cdot}75 . 10^{-7}$
	$1^2S_1 - 3^2P_1$	4593	$6{\cdot}33 . 10^{17}$	1/1	$1{\cdot}07 . 10^6$	$9{\cdot}35 . 10^{-7}$
	$1^2S_1 - 4^2P_2$	3877	$2{\cdot}53 . 10^{17}$	1/2	$3{\cdot}56 . 10^5$	$2{\cdot}81 . 10^{-6}$
	$1^2S_1 - 5^2P_2$	3612	$6{\cdot}86 . 10^{16}$	1/2	$1{\cdot}20 . 10^5$	$8{\cdot}33 . 10^{-6}$
	$1^2S_1 - 5^2P_1$	3617	$1{\cdot}37 . 10^{16}$	1/1	$4{\cdot}74 . 10^4$	$2{\cdot}11 . 10^{-5}$

The absorption measurements for sodium and cæsium are not by any means as accurate as for the mercury 2537 Å line, so that no great degree of accuracy can be claimed for the computed B's, A's, and τ's in these cases. In fact, the values of τ obtained by this method for sodium in the 2^2P_2 and 2^2P_1 states are distinctly high compared with those given by the methods already dealt with. In connection with the data for cæsium, it should be remembered that the atom in the higher states of excitation has other possibilities of spontaneous emission besides that corresponding to the reversal $nP \rightarrow 1S$. The values given under τ are merely the reciprocals of the A's, and for such cases do not represent the actual average life of the excited atom. Indeed, the average life of the atom in the $5P$ state of excitation is almost certainly less than that in a $3P$ state, although the τ's in the table might lead one to think otherwise.

Tolman has also calculated, from Füchtbauer's measurements on the absorption of the wave-length 5461 Å by iodine vapour, the probability of spontaneous reversal of the so excited iodine *molecule* to its original state. He finds an A of about 3.10^2 sec.$^{-1}$, but the life of the excited molecule must be much less than the reciprocal of this, since there are very many possibilities of spontaneous emission available for the excited molecule besides that which corresponds to the simple reversal of the absorption process. Again, the data of Imes for the infra-red absorption of HCl and HF have been used to compute the Einstein A's and B's referring to transitions of these molecules between different quantised states of rotation and vibration (in the absence of any electronic excitation). The small values found for these transition probabilities point to an average life of the quantum state of vibration-rotation of the molecule of the order 0·01 to 0·1 sec., a much larger life than that corresponding to any labile state of electronic excitation of an atom or molecule. Detailed figures for these cases need not be given, since the absorption data on which the calculations must be based hardly justify more than an estimate of the order of magnitude of the probability coefficients.

THE LIFE PERIOD OF THE EXCITED ATOM IN A METASTABLE STATE.

For the isolated atom in a metastable state of excitation, the possibility of spontaneous emission of radiation is by hypothesis excluded, and the life of the state is theoretically infinite. The appearance in the emission spectrum of a substance of "forbidden" lines which correspond to transitions from metastable to lower states of excitation can usually be ascribed to the disturbing action of strong electric or magnetic fields, invalidating the applicability of the Selection Rules. In the absence of such influences, and with spontaneous emission excluded, the actual period of existence of the atom in any metastable state is determined by (1) its collisions with other atoms, molecules, or electrons or with the walls of the containing vessel, (2) absorption of radiation by the metastable atom. As a result of collisions, the atom may either gain energy sufficient to bring it to a higher labile state, or it may lose the whole or part of its internal energy, the energy so lost appearing as internal energy of the colliding partner or as translatory energy of both colliding units. By absorption of radiation the metastable atom is transferred to a higher state of excitation, wherefrom it has other possibilities of transition by spontaneous emission besides that which would re-form the metastable state. The absorption by metastable mercury and helium atoms and the resulting fluorescent emission have already received brief mention. The specific nature of the reactions of the metastable state to collisions with other atoms and molecules will be dealt with in detail in another Chapter. Here, without entering more closely into the factors which determine the life of the atom in the metastable state, we may discuss the results of some recent measurements by Dorgelo (*Physica*, **5,** 429, 1925), by Dorgelo and Washington (*Verslag. Akad. Wetensch. Amsterdam*, **35,** 1009, 1926), and by Meissner and coworkers (*Physikal. Z.*, **26,** 687, 1925; *Ann. Physik*, **84,** 1009, 1927) upon the duration of the metastable states of mercury, neon, and argon. The principle of the experimental method is briefly as follows. The gas under investigation—say neon—is contained at a moderately low pressure (up to a few millimetres of Hg) in an absorption tube which can be excited intermittently by the positive part of an alternating current. By the side of this is another tube, also containing neon, which is intermittently induced to emit the characteristic lines of the neon spectrum by the negative part of the same alternating current. While the discharge passes through the absorption tube, an appreciable concentration of metastable neon atoms is built up therein. In the interval between successive excitations, these atoms are more or less rapidly deactivated by collision with other atoms or by diffusion to the walls of the tube. At some instant within this same interval the absorption tube is illuminated with the radiation from the emission tube, which radiation contains certain frequencies which metastable neon atoms can absorb. If at the moment of illumination an appreciable fraction of metastable atoms persists, these frequencies will be absorbed. However, if all the metastable atoms have returned to the normal state, no absorption of these frequencies is to be expected. By reducing the interval between the moment of cutting off the excitation of the absorption tube and the moment of illumination until absorption of these lines is first observed, the average life of the metastable state of the atom can obviously be obtained.

For the metastable 2^3P_0 state of the mercury atom, Dorgelo finds by this method a maximum life period of about $\frac{1}{200}$ sec. The presence of traces of hydrogen, however, appears to have a remarkable accelerating effect upon the decay of these and other metastable atoms. The "half-life" of the metastable 2^3P_0 state of argon at room temperatures and a pressure of 0·1 mm. Hg is about $3{\cdot}6 \times 10^{-3}$ sec. The case of the neon atom has been investigated in most detail by this method. For the neon atom the normal energy level and the first excited levels above the normal are as illustrated in Fig. 25. The s_3 and s_5 levels (old nomenclature) are both metastable, neither of these combining in emission or absorption with the normal p level. For the half-lives of these states in very pure neon at room temperature and a pressure of about 2 mm., Dorgelo has obtained the values $\frac{1}{2000}$ sec.

and $\frac{1}{240}$ sec. respectively. Here again, small traces of impurities, in especial of hydrogen, decrease the life of the metastable state very considerably. Dorgelo also finds that the life period of the s_5 state changes very considerably with the temperature. At 174° C. it is $\frac{1}{1550}$ sec., at — 196° C. it is about $\frac{1}{10}$ sec. This result suggests that, while the life of the atom in the higher metastable state s_3 is probably determined by collisions in which the atom loses energy, passing to the lower labile s_4 state or to the normal state, the life of the atom in the s_5 state depends upon the possibility of occurrence of a collision which will transfer it to the *higher* labile s_4 state. The difference in energy between s_5 and s_4 is about 0·05 volt or 1100 calories, and is the more frequently available in the form of energy of translatory motion of the colliding atoms the higher the temperature.

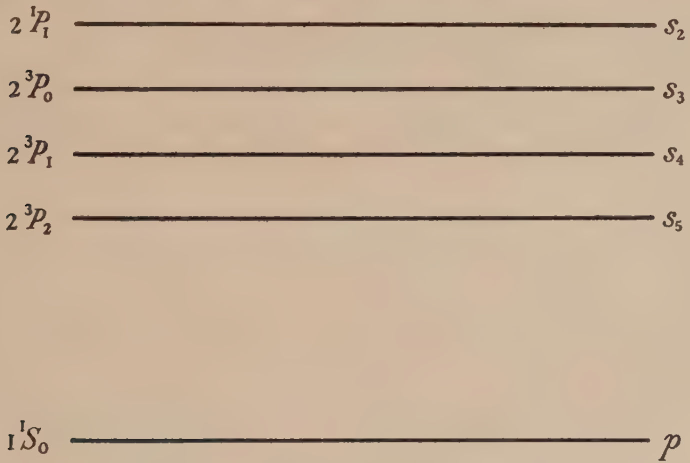

FIG. 25.—Energy levels of the neon atom.

Meissner and Graffunder (*Ann. Physik*, **84**, 1009, 1927) have confirmed Dorgelo's values for the lives of the metastable 2^3P_0 argon atom and the s_3 neon atom, but for s_5 neon they find at room temperature and 2 mm. pressure a much smaller half-life, viz. $5·6 \times 10^{-4}$ sec., than that obtained by Dorgelo. These authors have also made a special study of the dependence of the half-life of this state of the neon atom upon the pressure of the neon, with the following results :—

Pressure (mm. Hg) .	0·24	0·50	1·02	1·42	2·15	3·02	5·6
Half-life $\times 10^4$ (sec.) .	2·2	3·0	5·4	6·0	5·6	2·6	2·4

The life of the metastable state does not increase progressively with decreasing pressure, as might be anticipated, but goes through a maximum value at a pressure of about 2 mm. Hg. A similar optimum pressure of about 0·7 mm. is obtained for the metastable argon atom.

The suggested explanation of such an optimum pressure is that, whereas high pressures favour deactivation of the metastable atom by collision with other atoms, low pressures also favour deactivation by permitting of rapid diffusion to the walls of the containing vessel. Finally, we may mention that Meissner and Graffunder find the life of the metastable neon atom to be markedly lowered by intense illumination of the system with radiation which the metastable atoms themselves can absorb. This is, of course, what we should expect, since, following the act of absorption, other possibilities of deactivation by spontaneous emission are immediately available.

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CHAPTER IV.

MOLECULAR SPECTRA.

QUANTUM THEORY OF THE EMISSION AND ABSORPTION OF RADIATION BY MOLECULES.

The empirical facts regarding the characteristic band structure of molecular spectra have already been outlined in Chapter I.; particular examples of such spectra will be dealt with in the present Chapter. The complexity of most band spectra in the visible and in the ultraviolet has until recent years proved a serious obstacle to their detailed theoretical interpretation. However, a few of the vibration-rotation and pure rotation spectra lying in the near and far infra-red regions respectively possess a very simple structure, and, comparatively early in the history of the quantum theory, an attempt was made by Bjerrum (1912) to interpret such spectra by quantisation of the rotational and vibrational energy of the molecule. At that date, however, the view was still maintained that the occurrence of emission or absorption of radiation by a material medium necessarily implied that the responding vibrators should themselves possess a natural periodicity identical with that of the radiation involved. It was not until 1916 that the revolutionary concepts of Bohr were explicitly incorporated into the theory of band spectra by Schwarzschild. In the further development and systemisation of our knowledge in this field, the names of Heurlinger, Lenz, Kratzer, Birge, and Mulliken are specially prominent.

As in the case of atoms, what we may term the classical quantum theory, based on Bohr's two postulates and the Principle of Correspondence, meets with a very notable measure of success in explaining the major features of band spectra. Nevertheless, in regard to the finer details of both atomic and molecular spectra this classical quantum theory encounters the same fundamental difficulties—difficulties which are only partially avoided by abandoning the erstwhile restriction of quantum numbers to integral values. Fortunately, these difficulties for the most part disappear in the new quantum mechanics of Heisenberg and Schrödinger—especially in the wave-mechanics of the latter. Since, however, a rather complex mathematical treatment is necessary for the presentation of these new methods of quantisation, and since in the practical result the modifications involved are not often of serious consequence, it will be simplest to begin with the older methods of quantising molecular motion and to introduce the changes which the new mechanics demands only as these become necessary.

The stationary states and energy levels of the molecule are much more complex and diverse than those of the atom. This is due to the fact that, whereas the excitation of the atom can usually be referred to the displacement of a single electron relative to the atom residue, each such displacement of an electron in the molecule may be attended or coupled with a change in the state of vibration and in the state of rotation of the molecule. The theory of band spectra is essentially the theory of the quantisation of rotational and vibrational motion, and we will therefore begin with those spectra which are associated with changes in these modes of motion in the molecule without the added complication of electronic excitation. At the outset it may be remarked that considerations of space as well as of available data will compel us to restrict ourselves in the main to the spectra of diatomic molecules.

PURE ROTATION SPECTRA.

We will take the simplest of molecular models, the *rigid* diatomic dumb-bell model, and enquire into the possibilities of rotation of such a molecule about an axis through the centre of mass of the constituent atoms and perpendicular to the line joining them—the nuclear axis. This motion involves only one degree of freedom and a single variable co-ordinate, say the angle θ which the nuclear axis makes at any moment with some fixed axis of reference in the plane of rotation. The energy of rotation is purely kinetic. Any steady state of rotation implies, of course, a stationary state of constant rotational energy, this being given by

$$\text{rotational energy} = \tfrac{1}{2} I \omega_r^2 \quad . \quad . \quad . \quad . \quad (1)$$

where I is the moment of inertia of the molecule about the axis of spin, and $\omega_r\left(= \frac{d\theta}{dt}\right)$ is the angular velocity of spin. Without quantum restrictions, however, all values of ω_r are permissible, and as a consequence the energy of rotation E_r is continuously variable. The quantum equation of restriction which selects from this continuum the physically possible states of rotation is the Wilson-Sommerfeld relation $\oint p \, . \, dq = mh$, where m is a positive integer and q and p are the generalised co-ordinate and momentum referring to the degree of freedom concerned. With q equal to θ, the generalised momentum p becomes $I\omega_r$, the angular momentum of the spinning molecule, and the quantum equation of restriction takes the form

$$\int_0^{2\pi} I\omega_r \, . \, d\theta = mh,$$

leading to

$$I\omega_r = \frac{mh}{2\pi} \quad . \quad . \quad . \quad . \quad (2)$$

In passing it may be noted that this is the same restriction as was originally suggested by Bohr to fix the stationary states of rotation of an electron around a positive nucleus (cf. p. 57). The energy of rotation of the molecule in any quantised state of rotation is now restricted to one of the discrete series of values

$$E_m = \frac{m^2h^2}{8\pi^2 I} \, (m = 0, 1, 2, 3 \ldots) \quad . \quad . \quad . \quad . \quad (3)$$

and the permitted frequencies of rotation are

$$\nu_r = \frac{\omega_r}{2\pi} = \frac{mh}{4\pi^2 I} \quad . \quad . \quad . \quad . \quad (4)$$

These discrete frequencies of rotation of the molecule in its different stationary states, however, are not in the quantum theory to be identified with the frequencies of radiation which the molecule can emit or absorb in changing from one stationary state of rotation to another. To obtain the latter frequencies it is necessary to combine equation (3) with the Bohr frequency relation. By so doing, we obtain for the pure rotational spectrum of our hypothetical molecule the predicted series of lines expressed by

$$\nu = \frac{h}{8\pi^2 I}(m''^2 - m'^2),$$

where m' and m'' are the rotational quantum numbers of the two combining states of the molecule.

In regard to the actual emission or absorption of such radiation, however, we must distinguish sharply between homopolar and heteropolar molecules. If the constituent parts of the molecule, separated by the nuclear axis, carry electrical charges of opposite sign, the molecule is heteropolar ; it possesses an electric moment and can, by virtue of its rotation or capacity for rotation, emit or absorb radiation. In the absence of such polarity, however, reaction with radiation is excluded. Thus such diatomic molecules as HCl, HBr, and CO which are usually regarded as heteropolar should possess pure rotation spectra, whereas the homopolar molecules Cl_2, O_2, N_2, etc. should not be able to change their state of rotation (except in conjunction with some other change such as the displacement of an electron which might confer polarity on the molecule) by reaction with radiation. This distinction between heteropolar and homopolar units is fundamental to classical electrodynamical theory, and, by virtue of the Principle of Correspondence, it must hold to an equal degree in quantum mechanics. The Principle of Correspondence also limits considerably the frequencies which may be expected in the pure rotation spectrum of a heteropolar molecule. Taking three mutually perpendicular XYZ axes in space with the Z axis as the axis of rotation of the molecule, the X, Y, and Z components of the electric moment $\mathbf{P}$ of the dipolar molecule are expressed as Fourier expansions by

$$\mathbf{P}_x = \mathbf{P}\cos(2\pi\nu_r t + \phi)\ ;\ \ \mathbf{P}_y = \mathbf{P}\cos(2\pi\nu_r t + \phi)\ ;\ \ \mathbf{P}_z = 0.$$

Since only the fundamental frequency ν_r and not any of its overtones appears in these Fourier expansions for the components of $\mathbf{P}$ for any stationary state of rotation, it follows that the intensity of emission or of absorption of all lines, other than those for which the quantum number m changes by one unit only, should be vanishingly small. Accordingly, the frequencies of the lines in the pure rotation spectrum of a dipolar molecular are restricted to the values

$$\nu = \frac{h}{8\pi^2 I}(\overline{m + 1}^2 - m^2) = \frac{h}{8\pi^2 I} + \frac{h}{4\pi^2 I}\cdot m \quad . \quad . \quad (5)$$

$$(m = 0, 1, 2, 3\ .\ .\ .)$$

Thus the series of rotation frequencies should form an arithmetical progression.

The only pure rotation spectra of diatomic molecules which are available to test this result are those of the hydrogen halide gases, recently investigated by Czerny (*Z. Physik*, **34**, 227, 1925; **44**, 235, 1927). Each of these gases gives a far infra-red spectrum consisting of several absorption maxima, the frequencies (wave-numbers) of which form an approximate arithmetic progression. The positions of the maxima conform more accurately to the law

$$\nu = bm - dm^3 \quad . \quad . \quad . \quad . \quad (6)$$

where m is a variable integer and b and d are constants with $b \gg d$. The experimental values of b and d for the different halides are given in Table XV. The extent of agreement of the empirical equation (6) with observation is illustrated by Czerny's data for the HCl bands in Table XVI. Ignoring for the moment the points of discrepancy between (5) and (6), it is clear that the numerical factor b corresponds to the constant frequency difference $h/4\pi^2 I$ predicted by the simple theory. We may note here that the same constant difference $h/4\pi^2 I$

TABLE XV.

Gas.	Region of Absorption.	m.	b (cm.$^{-1}$).	d (cm.$^{-1}$).	I (c.g.s. units).	l (cm.).
HF	121-48 μ	2-5	41·142	$8{\cdot}69 \times 10^{-3}$	$1{\cdot}345 \times 10^{-40}$	$0{\cdot}923 \times 10^{-8}$
HCl	120-44 μ	4-11	20·832	$2{\cdot}09 \times 10^{-3}$	2·656 ,,	1·282 ,,
HBr	120-43 μ	5-14	16·697	$1{\cdot}39 \times 10^{-3}$	3·314 ,,	1·420 ,,
HI	130-86 μ	6-9	12·840	$8{\cdot}20 \times 10^{-4}$	4·309 ,,	1·616 ,,

between the frequencies of successive maxima is also predicted and occurs (to a first approximation) in the *near infra-red* rotation-vibration spectra of the hydrogen halides. By equating his empirical constant b to $h/4\pi^2 I$, Czerny has calculated the moment of inertia I and hence the linear separation l of the atoms in each hydrogen halide molecule. Table XV. gives for each gas the observed spectral region of far infra-red absorption, the range of m, the values of the constants b and d, and the therefrom calculated values of I and l.

TABLE XVI.

Far Infra-Red Absorption Bands of HCl ($b = 20{\cdot}832$, $d = 0{\cdot}00209$ cm.$^{-1}$)

m	4	5		7	8	9	10	11
$\nu_{\text{obsd.}}$	83·03	—	124·30	145·03	165·63	185·86	206·38	226·50 cm.$^{-1}$
$\nu_{\text{calc.}}$	83·19	103·80	124·54	145·10	165·58	185·96	206·22	226·36 cm.$^{-1}$

Equations (5) and (6) differ in respect of (α) the constant term $h/8\pi^2 I$ which is absent in the experimentally observed series, and (β) the small correction term in m^3 which is found to be necessary in the empirical equation. The theoretical significance of the latter term is as follows. In the derivation of equation (5), the molecule was for simplicity regarded as a perfectly rigid body in respect of rotation. There can be little question, however, that the actual molecule will undergo some slight deformation, involving an increase in its moment of inertia, when it is rapidly rotated. When proper allowance is made for the effect of rotation upon the molecular "constants," the expression (3) for the energy of the molecule in any stationary state of rotation becomes modified to

$$E_m = \frac{h^2}{8\pi^2 I_0}(m^2 - u^2 m^4) \quad . \quad . \quad . \quad (3a)$$

where I_0 is the moment of inertia in the rotationless state, and $u = \dfrac{h}{4\pi^2 I_0} \cdot \dfrac{1}{\nu_v}$ is a constant determined by I_0 and by ν_v, the natural frequency of vibration of the atoms in the molecule with respect to one another. Naturally, the stronger the binding of the two atoms in the molecule, the greater is ν_v and the smaller is u. The modified series of absorbed frequencies in the far infra-red derived from (3a) with the same restriction principle $\Delta m = 1$ as before is now

$$\nu = \frac{h}{8\pi^2 I_0}(2m + 1) - \frac{h}{8\pi^2 I_0} u^2(\overline{m + 1}^4 - m^4) \quad . \quad (5a)$$

In this equation the small correction term is primarily a function of m^3, and it is of the right order of magnitude, since for HCl the value of u^2 calculated from the known values of I_0 and ν_v is about 5×10^{-5}, whereas the empirical constant d in (6) entails for HCl a value of u^2 which is also about 5×10^{-5}.

The fact that the empirical expression (6) for the series of far infra-red absorption maxima lacks a constant term which would correspond to the predicted constant term $h/8\pi^2 I$ cannot be explained so easily. We may defer consideration of this discrepancy until we have indicated how a similar discrepancy obtains between the observed and the predicted absorption frequencies of the hydrogen halides in the *near* infra-red.

VIBRATION-ROTATION SPECTRA OF DIATOMIC MOLECULES.

Simultaneously with rotation of the dipole molecule as a whole round one of its principal axes, a linear vibration of the constituent atoms with respect to one another is possible. For small amplitudes of vibration this motion will be very nearly simple harmonic in character. Writing the natural frequency of vibration equal to ν_v, the Sommerfeld-Wilson equation of restriction applied to the degree of freedom of vibration restricts the vibrational energy to one of the discrete series of values

$$E_p = ph\nu_v \; (p = 0, 1, 2, 3 \ldots) \qquad . \quad . \quad (7)$$

where p is the vibration quantum number. Combining this with (3), the total energy of the dipole in the stationary state (p, m) is given by

$$E_{p, m} = ph\nu_v + \frac{m^2h^2}{8\pi^2 I} \qquad . \quad . \quad . \quad (8)$$

and, from the Bohr frequency relation, the molecule should emit or absorb the frequency

$$\nu = \nu_v(p'' - p') + \frac{h}{8\pi^2 I}(m''^2 - m'^2)$$

in passing between the stationary states (p', m') and (p'', m''). However, for motion which is a combination of simple harmonic vibration along one axis and rotation about a perpendicular axis, the transitions which may be accompanied by emission or absorption of radiation are limited to those for which $\Delta p = 0$ or 1 and $\Delta m = 1$. Confining our attention to absorption, it is obvious that the condition $\Delta p = 0$, $\Delta m = 1$ gives the pure rotation spectrum already considered. The near infra-red absorption spectrum derives from a change in the vibration quantum number of one unit and a simultaneous change in the rotation quantum number of one unit, and since in absorption the latter can either increase or decrease while the former increases, we have to take account of the two possibilities $m'' - m' = +1$ and $m'' - m' = -1$. From these are predicted the following absorption frequencies:—

$$\nu = \nu_v \pm \frac{h}{8\pi^2 I}(2m + 1) \quad . \quad . \quad . \quad (9)$$
$$(m = 0, 1, 2, 3 \ . \ . \ .)$$

This scheme of near infra-red frequencies is shown diagrammatically in Fig. 26. The dotted line represents the missing * central line of frequency ν_v, that denoted by 1 → 2 represents the line absorbed when $m = 1$ *increases* by one unit, that denoted by 2 → 1 the line absorbed when $m = 2$ *decreases* by one unit in the transition, and so on. Clearly the frequencies of the predicted lines form an arithmetical progression with a constant difference $\Delta\nu = \frac{h}{4\pi^2 I}$ which is identical with that in the pure rotation spectrum of the same molecule.

The most extensively studied of near infra-red absorption bands of diatomic gases are those of the hydrogen halides. For the purposes of comparing the above result with observation, we may take the absorption band of HCl with centre at 3·46 μ which is more or less representative of all. The fine structure of this band is illustrated in Fig. 7, and its chief characteristics have already been described. The observed absorption maxima form an arithmetic progression (on the frequency or wave-number scale) only to a first approximation, but the actual convergence of the maxima in the direction of increasing frequency is fairly slow, and in the neighbourhood of the centre of the band the spacing agrees very well in absolute value with the spacing of the absorption maxima in the far infra-red series of the same gas ($\Delta\nu = \frac{h}{4\pi^2 I} = 20{\cdot}6$ and $20{\cdot}8$ cm.$^{-1}$ in the two cases). The departure of the observed maxima from uniform spacing is expressed by the quadratic and cubic terms in m in the empirical expression for the frequencies given by Colby :—

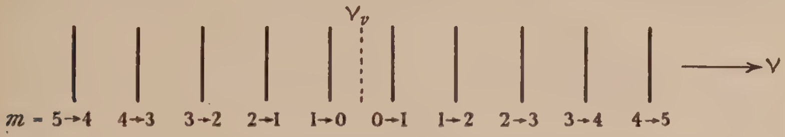

FIG. 26.—Predicted structure of near infra-red absorption band.

$$\nu = 2886{\cdot}07 \pm 20{\cdot}6\, m - 0{\cdot}301\, m^2 \mp 0{\cdot}00206\, m^3.$$

Here the cubic term in m^3 is of the same order of magnitude as, and can be identified with, the corresponding term in Czerny's equation (6) for the far infra-red frequencies. However, this correction term,

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[*] Only when the vibration has a component along the axis of rotation does the Correspondence Principle permit of a change of vibration quantum number unaccompanied by a change in the rotation quantum number, which would lead to absorption of the frequency ν_v itself.

which takes account of the slight "give" of the molecule in rotation, is of minor significance in the present case compared with the term in m^2 which essentially controls the departure of the near infra-red lines from regular spacing. The presence of this term suggests that it may not be strictly legitimate to ignore the mutual action of vibration and rotation upon one another as we have done in deriving equation (9). Neither may it be permissible to treat the nuclear vibration itself as a pure simple harmonic motion—indeed, direct experimental evidence of the *anharmonic* motion of the oscillator is in the present case afforded by the observation of overtone bands at 1·76 μ and 1·19 μ. Reserving these points for future discussion, however, the most serious discrepancy between prediction and observation lies in the obvious and complete absence of one line of the progression—at the position of anomalous spacing in the centre of the band. This missing line must not be confused with the central line ν_v which would correspond to a transition in which m remained unchanged, and which is naturally excluded (cf. footnote on p. 181). The fairly symmetrical distribution of intensity of absorption on either side of the gap naturally suggests that the frequency ν_v is located there, but the anomalous spacing requires that one or other of the predicted lines $1 \rightarrow 0$ or $0 \rightarrow 1$ of Fig. 26 must also be absent. Originally this presumed missing line in absorption was identified with that corresponding to the quantum change $m = 0 \rightarrow m = 1$ and various ingenious but not too plausible reasons for its non-appearance were proposed. An alternative suggestion, first put forward by Einstein, was that there is no real discrepancy between theory and observation, but that the apparent anomaly owes its origin to an improper assignment of integral values to the rotation quantum number m of equation (9). If m be restricted to *half-integral* instead of integral values, viz.

$$m = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2} \dots,$$

equation (9) becomes modified to

$$\nu = \nu_v \pm \frac{h}{4\pi^2 I} \cdot m_1 \qquad \dots \qquad (9a)$$

$$(m_1 = 1, 2, 3, 4 \dots)$$

where m_1 is written for $\frac{1}{2}(2m + 1)$ and is integral. The series of frequencies (9*a*) leads naturally to a double spacing of $2\Delta\nu$ at the centre of the band in agreement with observation.

Such a restriction of the quantum number m to half-integral values also serves to remove the discrepancy already noted between the predicted frequencies of the far infra-red absorption spectrum and the experimental series of Czerny, as is immediately obvious when equation (5) or (5*a*), with $2m_1$ substituted for $(2m + 1)$, is compared with Czerny's relation (6). It would appear, then, that from the practical standpoint Einstein's suggestion deserves further consideration. A physical interpretation of the appearance of half-quantum numbers in this connection has been offered by Kratzer. The assumption that m is half-integral implies, of course, that the nuclear angular momentum of the molecule about its axis of rotation is not expressed by one of the values 0, $\frac{h}{2\pi}$, $\frac{2h}{2\pi}$, $\frac{3h}{2\pi}$, etc., but by one of the values $\frac{1}{2}\cdot\frac{h}{2\pi}$, $\frac{3}{2}\cdot\frac{h}{2\pi}$, $\frac{5}{2}\cdot\frac{h}{2\pi}$, etc. The *total* angular momentum of the molecule about this axis of rotation may, however, still be an integral multiple of $h/2\pi$ if, in addition to the nuclear angular momentum, there is also a resultant *electronic* angular momentum about the same axis, in amount equal to $\frac{1}{2}\cdot\frac{h}{2\pi}$. Such a residual angular momentum would have to be compounded with the nuclear angular momentum to give the total angular momentum of rotation of the molecule. Despite the fact that in certain molecules there may well be a residual angular momentum of the type postulated due to electron spins, the *ad hoc* nature of the assumption in the present case leaves something to be desired, and it is gratifying that in the new quantum mechanics the use of half-integral values of m, at least for the rotation of polar molecules, does not appear to be necessary.

In the *Schrödinger wave-mechanics*, the expression (2) for the angular momentum of the dipole rotator becomes modified to

$$I\omega_r = \frac{h}{2\pi}\sqrt{m(m+1)} \quad . \quad . \quad . \quad (10)$$

where the symbols retain their previous meaning. The permitted values of the quantum number m are 0, 1, 2, 3, 4, . . . It follows from equation (1) that the energy of rotation E_m should become

$$E_m = \frac{h^2}{8\pi^2 I}m(m+1) \quad . \quad . \quad . \quad (11)$$

Using the Bohr frequency condition in conjunction with this, the two series of far infra-red and near infra-red absorption frequencies are then given by

$$\left.\begin{aligned} \nu &= (m+1)\frac{h}{4\pi^2 I} \\ \text{and} \qquad \nu &= \nu_v \pm (m+1)\frac{h}{4\pi^2 I} \end{aligned}\right\}(m = 0, 1, 2, 3, 4 \ldots) \quad . \quad (12)$$

respectively.

But for the absence of the small correction terms in m^2 and m^3, these relations are in formal agreement with observation. The same series are, of course, alternatively expressed by the equations

$$\left.\begin{aligned} \nu &= m \cdot \frac{h}{4\pi^2 I} \\ \text{and} \qquad \nu &= \nu_v \pm m \cdot \frac{h}{4\pi^2 I} \end{aligned}\right\}(m = 1, 2, 3 \ldots)$$

where the minimum value of the series variable is taken as unity instead of zero. It may also be noted here that in the new wave mechanics an expression different from (7) is obtained for the energy of nuclear vibration of the strictly harmonic oscillator. The modified expression is

$$E_p = (p + \tfrac{1}{2})h\nu_v \quad . \quad . \quad . \quad . \quad (13)$$

where the quantum number p is integral. This addition of a constant term $\frac{1}{2}h\nu_v$ to the vibrational energy, however, has obviously no effect upon the optical frequencies emitted or absorbed by the harmonic oscillator, since these frequencies are determined by energy differences.

We now revert to a closer discussion of the anharmonic nature of the nuclear vibration and of the mutual action of the vibration and rotation of the molecule upon one another, which together must be held responsible for the asymmetry of the two branches of the near infra-red absorption band of Fig. 7. As already mentioned, proof of the anharmonic nature of the nuclear vibration in the HCl molecule is found in the fact that besides the main absorption band with centre at 3·46 μ, there are also two overtone bands of essentially the same fine structure with centres at 1·76 μ and 1·19 μ. These bands obviously derive from changes in the vibration quantum number p of two and three units respectively—changes which would be forbidden by the Principle of Correspondence if the vibration were strictly harmonic. Additional evidence of the anharmonic nature of the vibration is afforded by the fact that while the frequencies of the three band centres are nearly, they are not exactly in the ratio 1 : 2 : 3. This is taken account of in the following way. For the non-rotating *anharmonic* oscillator in any quantised state of vibration, the expression (13) for the energy of vibration becomes modified to

$$E_p = (p + \tfrac{1}{2})h\nu_v'\{1 - (p + \tfrac{1}{2})x' + \ldots\} \quad . \quad . \quad (14)$$

where ν_v' is the vibration frequency of the oscillator for a vanishingly small amplitude of vibration, and x' is a small constant determined by the exact nature of the forces which hold the molecule together. The expansion within the brackets advances in powers of $(p + \frac{1}{2})x'$, but the terms of higher power than the first are for most purposes negligible. It easily follows from (14) that the central frequencies of the absorption bands which would correspond to the quantum jumps $p = 0$ to $p = 1$, 2, and 3 are now not exact overtones, but are given by

$$\nu_v'(1 - 2x'),\ 2\nu_v'(1 - 3x'),\ \text{and}\ 3\nu_v'(1 - 4x')$$

respectively. The frequency interval between successive band centres should therefore decrease slightly as the frequency increases, in agreement with observation.

The principal effect of rotation upon the anharmonic oscillator is to modify the position of equilibrium of the nuclei in the molecule and therefore the strength of the chemical bond. Without entering into details, the result is that the total energy of the molecule in the state

(p, m) differs from its energy—cf. equation (14)—in the state $(p, 0)$, not only by the amount of rotational energy E_m, but also by a small term which to a first approximation is proportional to the first power of p and to the second power of m, viz.

$$E_{p,m} = E_{p,0} + \frac{h^2}{8\pi^2 I} m(m+1) - h\alpha p m^2 \quad . \quad . \quad (15)$$

The constant α depends upon the moment of inertia I and also upon the law of force between the nuclei. It is usually positive and increases as the vibration becomes more anharmonic. Considering now the absorption frequencies which result from the two transitions $(0, m-1) \rightarrow (1, m)$ and $(0, m) \rightarrow (1, m+1)$ and which correspond to two consecutive absorption maxima in the same near infra-red band, these are respectively *

$$\nu = \nu_v + \frac{h}{4\pi^2 I} \cdot m - \alpha m^2$$

and

$$\nu = \nu_v + \frac{h}{4\pi^2 I}(m+1) - \alpha(m+1)^2.$$

The separation of consecutive absorption maxima is therefore

$$\Delta\nu = \frac{h}{4\pi^2 I} - \alpha(2m+1) \quad . \quad . \quad . \quad (16)$$

and, α being $+^{ve}$, this decreases systematically as m increases, that is, as we pass from left to right of the positive branch of the band. It is easy to see from a consideration of the transitions $(0, m) \rightarrow (1, m-1)$ and $(0, m+1) \rightarrow (1, m)$ that $\Delta\nu$ should *increase* systematically as m increases in the negative branch of the band. In this way is explained the regular convergence of the absorption maxima within each band in the direction of increasing frequency which is observed not only in the vibration-rotation absorption bands of HCl but also in those of HBr and HF.

INFRA-RED ABSORPTION SPECTRA OF POLYATOMIC MOLECULES.

Such molecules possess two or three principal axes of rotation and accordingly two or three different moments of inertia. The general rotation of an unsymmetrical body is doubly periodic and two rotational quantum numbers are therefore required in defining any stationary state. For mathematical treatment, the simplest case is that of the symmetrical top molecule, the polyatomic molecule with two of its three moments of inertia equal. For the stationary state of rotation defined by the two rotational quantum numbers

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* The slight variation of I with m, which would introduce a small correction in m^3, is here ignored (cf. p. 181).

m_1 and m_2, the energy of rotation is, on the basis of the new wave mechanics, given by

$$E = \frac{h^2}{8\pi^2}\left\{\frac{1}{A}(m_1^2 + m_1) + \left(\frac{1}{C} - \frac{1}{A}\right)m_2^2\right\} \quad . \quad (17)$$

$$\left\{\begin{matrix} m_1 = 0, 1, 2, 3 \ldots \\ m_2 = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm m_1 \end{matrix}\right\}$$

where A and C are the principal moments of inertia of the molecule. The possible changes in the rotational quantum numbers for transitions accompanied by absorption of radiation are primarily limited to $\Delta m_1 = 0$ and ± 1, $\Delta m_2 = 0$ and ± 1. In special cases changes in m_1 or m_2 may be even further restricted, depending upon the disposition of the polarity of the molecule relative to the principal axes of rotation. The absorption frequencies corresponding to $\Delta m_1 = \pm 1$, $\Delta m_2 = 0$ obviously form an arithmetic progression of lines with spacing $\Delta\nu = \frac{h}{4\pi^2 A}$; those corresponding to $\Delta m_1 = 0$, $\Delta m_2 = \pm 1$ form another progression of lines with spacing $\Delta'\nu = \frac{h}{4\pi^2}\left\{\frac{1}{C} - \frac{1}{A}\right\}$. If simultaneous change of both quantum numbers is permitted, i.e $\Delta m_1 = \pm 1$, $\Delta m_2 = \pm 1$, then each of the " lines " of the first mentioned progression becomes itself a progression of lines with spacing $\Delta'\nu$. From this it will be clear that the vibration-rotation bands of polyatomic molecules may well exhibit a very complex fine structure. The near infra-red absorption bands of CO_2, H_2O, and NH_3 very probably belong to the category discussed. The fine structure of certain of the infra-red bands of ammonia, for example, is explicable in terms of two different spacing constants $\Delta\nu$ and $\Delta'\nu$. In hardly a single case, however, have the sub-maxima within an absorption band of a polyatomic molecule been sufficiently well systematised to warrant quantitative discussion.

The centre of each near infra-red absorption band represents the frequency which the molecule would absorb in changing its state of vibration without simultaneously changing its state of rotation. For the dipolar anharmonic oscillator with a single normal frequency of vibration the totality of near infra-red band centres consists of the one fundamental and one or more overtone frequencies. The polyatomic molecule, however, has usually more than one normal frequency of internal vibration of its constituent parts about their equilibrium positions, and correspondingly there should be bands in its near infra-red spectrum representing several fundamental frequencies, several overtones of each fundamental (provided the vibrations are anharmonic), and also several combination overtones. Denoting the fundamental frequencies by ν_1, ν_2, ν_3, etc., and ignoring the factors due to the anharmonic nature of the vibrations, the complete series of band centres should be represented (approximately) by the frequencies

$$\nu = \tau_1\nu_1 + \tau_2\nu_2 + \tau_3\nu_3 + \ldots$$

where τ_1, τ_2, τ_3, etc. are variable $+^{\text{ve}}$ or $-^{\text{ve}}$ integers. Of the several examples of such series which have been encountered we may cite one or two in detail. The infra-red absorption spectrum of acetylene gas consists of three fundamental bands with centres at 13·77, 7·54, and 3·07 μ, and two other bands at 3·77 and 2·52 μ, the one of which is an almost exact harmonic of the band at 7·54 μ, while the other is a combination overtone of the first and third fundamentals. Again, ether vapour possesses three absorption bands at 10·7, 8·8, and 6·9 μ which apparently correspond to fundamental vibrations in the molecule. At 4·75 μ there is another band which is a simple combination overtone of the first two, while further bands at 3·45 and 2·5 μ are the first and second harmonics of the bands at 6·9 μ. Finally, the numerous absorption bands of water vapour lying between 6·3 μ and 0·7 μ are the harmonics and combination overtones of the two fundamental bands at 6·26 μ and 2·66 μ, their wave-numbers being expressed by the relation

$$\nu = 1597\tau_1 + 3760\tau_2.$$

In this formula 1597 cm.$^{-1}$ and 3760 cm.$^{-1}$ are the wave-numbers corresponding to the wave-lengths 6·26 μ and 2·66 μ. The extent of agreement between the calculated and the observed wave-lengths of the band-centres in this case is shown in Table XVII.

TABLE XVII.

NEAR INFRA-RED ABSORPTION BANDS OF WATER VAPOUR.

τ_1 τ_2	1 0	0 1	2 0	1 1	0 2	3 0	2 1	1 2	3 1	2 2	1 3	0 4
λ (calc.)	—	—	3·13	1·87	1·33	2·09	1·44	1·10	1·17	0·93	0·78	0·67
λ (obsd.)	6·26	2·66	3·15	1·87	1·37	2·05	1·46	1·13	1·16	0·94	0·77	0·69

THEORY OF ELECTRONIC BAND SPECTRA.

We have so far confined our attention to the simpler types of molecular spectra lying in the infra-red which are found to be associated with transitions of the molecule between different rotational or rotational-vibrational energy levels. In addition to the comparatively low excitation levels hereby involved, however, the molecule is usually capable also of assuming a number of much higher energy levels corresponding to electronic excitation, that is, to displacement of one of the peripheral electrons of the molecule from its normal to some outer orbit. Emission or absorption lines in the visible or ultraviolet spectrum of the molecule derive primarily from transitions between these electronic energy levels. The fact that molecular spectra in these regions are usually of extreme complexity is due to the circumstance that every main electronic energy level of the molecule naturally divides into a great number of sub-levels, corresponding to the various states of vibration and rotation which may be associated with the same electronic configuration. In changing its electronic state, the molecule can simultaneously alter its state of vibration and rotation, hence it sometimes happens that one and the same electronic jump in the molecule (which in the case of an atom would give a single spectral line) is actually associated with as many as a hundred emission bands, each of which in turn may contain hundreds of individual lines.

The totality of lines in the complete emission or absorption spectrum of a molecule segregate primarily into bands. The bands themselves may be classified into progressions and sequences, or more generally into groups which include related progressions and sequences. Finally, some systematisation of the different groups of bands belonging to one and the same emitting or absorbing unit appears to be possible in the light of recent investigations. Fantastic as it may seem, each group of related bands in the molecular spectrum, although it may contain thousands of individual lines, corresponds formally to the single line or multiplet in the spectrum of an atom. The line, the band, and the band group are interpreted in terms of the quantum theory in the following way. Different electronic transitions of the molecule produce different groups of bands * ; different changes in the vibrational state of the molecule accompanying the same electronic transition give the numerous bands which belong to the same group ; and finally different changes in the state of rotation of the molecule coupled with the same electronic and vibrational transitions result in the multiplicity of lines within one and the same band.

Very little detailed spectroscopic knowledge is available for molecules composed of more than two atoms, so that we must restrict ourselves for the most part to a discussion of the electronic band spectra of diatomic molecules only. The first point to note is that, whereas rotation and rotation-vibration spectra are confined to heteropolar molecules, this limitation no longer applies when the *electronic* configuration of the molecule changes in transitions between stationary states. The primary condition for the emission or absorption of radiation imposed by the Correspondence Principle is that the material unit in at least one of the two combining states should possess an electric moment. This condition is not satisfied by the homopolar molecule in any state of vibration or rotation, but as soon as one of its peripheral electrons is displaced from its normal orbit the so excited molecule acquires an electric moment and becomes heteropolar. Hence, although the normal molecule of nitrogen cannot alter its state of rotation or vibration by absorption in the infra-red, it can do so by absorption in the ultra-violet when the transition implied is accompanied by a simultaneous electron jump in the molecule.

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* The actual number of band groups in any molecular spectrum is very limited, a fact which would appear to indicate that there are only a very few states of electronic excitation which the molecule can assume without disruption into its constituent parts.

As with the atom, each energy level of the molecule is to be represented as a function of a set of quantum numbers. For the diatomic molecule, one of these m is sufficient to characterise the state of rotation, and another p the state of vibration. The remaining quantum numbers are characteristic of the electronic configuration of the molecule in the stationary state under consideration. In general, we may expect by analogy with the case of the atom that more than one quantum number will be required to specify the orbit of the optical electron. Indeed, recent work on band spectra points to the conclusion that the energy levels associated with the valency electrons of molecules correspond in all essentials (enumeration, multiplicity, etc.) with the levels associated with the valency electrons of atoms, and on this basis a complete systematisation of the electronic energy levels of molecules is now in process of development. With this, however, we are not at present concerned, our problem at the moment being to interpret the spacing of the lines which form a single molecular band and the spacing of the bands which form a single band group in terms of the vibrational and rotational quantum numbers of the molecule in the two combining states. For ease of reference, it will be convenient to specify each main electronic energy level of the molecule in a purely formal manner by a single electronic quantum number n. Taking account of rotation and vibration, the total energy of the molecule in any stationary state is then a function of the three integers n, p, and m, viz. $E(n, p, m)$. This total energy may conveniently be split up into three parts, thus—

$$E(n, p, m) = E_n + E_p + E_m \quad . \quad . \quad . \quad (18)$$

representing the electronic, vibrational, and rotational contributions respectively, but, by so doing, a certain amount of care is necessary in defining the exact meaning of these component terms. The molecular " constants "—the natural frequency of vibration ν_v of the atoms with respect to one another and the moment of inertia I of the molecule—depend upon the forces which hold the molecule together, which in turn depend upon the electronic configuration of the molecule. This imposes a very marked dependence of E_p and E_m upon the electronic quantum number n, which must be taken account of in the mathematical expressions for these terms. There must, of course, also be some reciprocal influence of rotation and vibration upon the electronic configuration itself, but this is not likely to be appreciable, and, in the absence of any exact knowledge of the nature of the function E_n, such an effect must be omitted from further consideration.

The frequency of monochromatic radiation which the molecule absorbs in passing from the state (n', p', m') to the state (n'', p'', m'') or emits * in the reverse transition ($n'' > n'$) is given by

$$\nu = \frac{E_{n''} - E_{n'}}{h} + \frac{E_{p''} - E_{p'}}{h} + \frac{E_{m''} - E_{m'}}{h} \quad . \quad . \quad (19)$$

We shall write the first term equal to ν_n. This is nearly, but not exactly, equal to the optical frequency which would be absorbed or emitted if the change in the electronic configuration occurred without accompanying changes in the states of rotation and vibration (cf. p. 195). As regards the second term we may at once assume that the vibration of the atoms in the molecule in one or both of the two combining states is anharmonic. Accordingly $E_{p'}$ and $E_{p''}$ are given by the equations

$$E_{p'} = (p' + \tfrac{1}{2})h\nu_v'\{1 - (p' + \tfrac{1}{2})x'\} \quad . \quad . \quad (20a)$$

and

$$E_{p''} = (p'' + \tfrac{1}{2})h\nu_v''\{1 - (p'' + \tfrac{1}{2})x''\} \quad . \quad . \quad (20b)$$

where ν_v' and ν_v'' are the natural frequencies of vibration (for vanishingly small amplitudes of vibration) of the molecule in the electronic conditions specified by n' and n'' respectively, and x' and x'' are the corresponding "anharmonic constants" of the motion. Finally, with I' and I'' for the moments of inertia of the molecule in its lower and upper states, the rotational energy terms are given by

$$E_{m'} = \frac{h^2}{8\pi^2 I'} m'(m' + 1) = h \, . \, B' \, . \, m'(m' + 1) \quad . \quad . \quad (21a)$$

and

$$E_{m''} = \frac{h^2}{8\pi^2 I''} m''(m'' + 1) = h \, . \, B'' \, . \, m''(m'' + 1) \quad . \quad (21b)$$

Making these substitutions, equation (19) becomes

$$\nu = \nu_n + [(p'' + \tfrac{1}{2})\nu_v''\{1 - (p'' + \tfrac{1}{2})x''\} - (p' + \tfrac{1}{2})\nu_v'\{1 - (p' + \tfrac{1}{2})x'\}] + B''m''(m'' + 1) - B'm'(m' + 1) \quad . \quad . \quad (22)$$

Examining the vibrational and rotational changes from the point of view of the Correspondence Principle, it is found that no limitation is imposed upon the value of Δp in absorption or in emission if the vibration in one or both of the combining states is anharmonic. Changes in the rotational quantum number, however, are still normally restricted to $\Delta m = \pm 1$. In addition, however, where the molecule possesses a resultant electronic angular momentum round the axis of rotation, it can change its state of electronic and vibrational excitation without any alteration of its state of rotation; that is, in this particular case $\Delta m = 0$ is also allowed in emission and in absorption.

We can now interpret by means of equation (22) the series relations

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* In what follows we consistently use (n', p', m') and (n'', p'', m'') as the quantum numbers of the lower and the upper states of excitation of the molecule respectively. This convention implies $n'' > n'$, but not necessarily $p'' > p'$ or $m'' > m'$.

of the individual lines within a simple electronic band, and also the progressions and sequences which the bands of any group form.

Structure of the Electronic Band.—For all the lines of a single band the quantum numbers (n', p') and (n'', p'') of the two combining states of the molecule remain the same, and only the rotation quantum numbers m' and m'' vary. This variation is subject to one or other of the conditions $m'' = m' \pm 1$ or $m'' = m'$. If we neglect the small mutual effects of vibration and rotation, the ν_v's and the x's of equation (22) remain constant for the band, and the equation can therefore be written in the form

$$\nu = \nu_{np} + B''m''(m'' + 1) - B'm'(m' + 1) \quad . \quad . \quad (23)$$

where $\nu_{np} = \nu_n + [\ .\ .\ .].$

Taking the change $m'' = m \rightarrow m' = m - 1$ *in emission*, the possible emission frequencies corresponding to possible values of the parameter m are given by

$$\nu = \nu_{np} + B''m(m + 1) - B'(m - 1)m$$

or

$$\nu = \nu_{np} + (B'' + B')m + (B'' - B')m^2.$$

On the other hand, for the change $m'' = m - 1 \rightarrow m' = m$, *also in emission*, the various frequencies are represented by

$$\nu = \nu_{np} - (B'' + B')m + (B'' - B')m^2.$$

Both sets of emission frequencies, then, which may result from the transition $(n'', p'') \rightarrow (n', p')$ are included in the one equation

$$\nu = \nu_{np} \pm (B'' + B')m + (B'' - B')m^2 \quad . \quad . \quad (24)$$

Provided the molecule has no intrinsic angular momentum about the nuclear axis (due to electron orbits), the rotational quantum number m is any positive integer, zero included. Accordingly, the parameter m in the above equation is also any positive integer, with however, zero excluded, since we have taken the rotational state of quantum number $(m - 1)$ as one of the combining states in deriving (24).

For an *absorption* band, it will be obvious that the frequencies absorbed in the reverse transitions $(n', p') \rightarrow (n'', p'')$ with $m - 1 \rightleftharpoons m$, are represented by the same equation, the positive sign now referring, however, to an increase in the rotational quantum number from $m - 1$ to m, the negative sign to a decrease from m to $m - 1$ as a result of the act of absorption. It should be emphasised that, both in absorption and in emission, we take the coefficient B'' to refer always to the state of higher *total* energy content of the molecule, whether or not this be the state of higher rotational energy also.

Comparing equation (24) with the empirical equations (cf. p. 35, Chapter I.) which are found to express the frequencies of the R and P branches of the simplest electronic emission bands, viz.

$$\left.\begin{array}{l} R \text{ branch}: \ \nu = a_1 + b_1 m + c_1 m^2 \\ P \text{ branch}: \ \nu = a_1 - b_1 m + c_1 m^2 \end{array}\right\} (m = 1, 2, 3, 4 \ .\ .\ .),$$

it appears that in emission any line of the R or positive branch must derive from a change of state of the molecule involving a decrease of one unit in the rotational quantum number, while any line of the P or negative branch must derive from a change involving an increase of one unit in this quantum number. The reverse, of course, holds for absorption. The empirical constants a_1, b_1, and c_1 of the band are to be identified with ν_{np}, $(B'' + B')$, and $(B'' - B')$ respectively. The frequency of the missing line at the point of junction of the R and P branches (cf. Fig. 8) is $\nu = a_1 = \nu_{np}$. This line is naturally excluded in the theoretical expression (24).

Depending upon the value of c_1 an important theoretical distinction can now be drawn between electronic bands which degrade towards the red and those which degrade towards the violet. For the former, the empirical constant c_1 and therefore also $(B'' - B')$ is negative; for the latter, positive. Remembering that $B = \frac{h}{8\pi^2 I}$ and that B'' always refers to the state of higher total energy content of the molecule, it follows that for emission or absorption bands shaded towards the red $I'' > I'$, that is, the moment of inertia of the molecule and therefore also its linear dimensions increase when its electronic energy level is raised. Conversely, shading of a band towards the violet means that the moment of inertia or nuclear separation of the molecule decreases when its electronic energy level is raised.

From the actual values of b_1 and c_1 in the empirical expression for the lines of any band, the constants B' and B'' can be derived, and hence the moments of inertia of the molecule in the two combining states. For example, the cyanogen emission band at 3883 Å (one of the violet group of cyanogen bands) consists of a positive and a negative branch, the lines of which are closely represented (in wave-numbers) by the equation

$$\nu = \nu_{np} \pm 3{\cdot}84m + 6{\cdot}8 \times 10^{-2}\, m^2.$$

Comparing this with equation (24), it follows that $B' = 1{\cdot}89$ and $B'' = 1{\cdot}95$, from which we derive $I' = 1{\cdot}47 \times 10^{-39}$ and $I'' = 1{\cdot}41 \times 10^{-39}$ c.g.s. units. The moments of inertia of the molecule in the two states differ then by about 4 per cent., the higher value corresponding to the lower state of excitation, in accord with the degradation of the band towards the violet. The linear dimensions (separation of the atoms) of the CN molecule in the two states of excitation responsible jointly for the emission of the 3883 Å band are easily computed from the above values of I' and I'' to be $1{\cdot}17 \times 10^{-8}$ and $1{\cdot}15 \times 10^{-8}$ cm. respectively.

The Q or zero branch, which is sometimes superimposed upon the R and P branches of a band, corresponds in theory to change in the electronic and vibrational states of the molecule without accompanying change in the rotational state. Putting m'' equal to m', equation (23) becomes

$$\nu = \nu_{np} + (B'' - B')m'(m' + 1),$$
$$(m' = 0, 1, 2, 3, \ldots)$$

or, changing from the variable m' to the variable $m = m' + 1$ (a change which of course does not affect the general nature of the relation but only increases the minimum value of the independent variable by one unit)

$$\nu = \nu_{np} + (B'' - B')(m - 1)m \qquad (m = 1, 2, 3, 4 \ldots)$$

In order to compare this with the empirical equation (25) of Chapter I. for the zero branch frequencies, a further slight modification in its algebraic form is necessary. The factor $(m - 1)m$ may be re-written as $(m - \frac{1}{2})^2 - \frac{1}{4}$, hence

$$\nu = \nu'_{np} + (B'' - B')(m - \tfrac{1}{2})^2 \quad . \quad . \quad . \quad (25)$$

where $\nu'_{np} = \nu_{np} - \frac{1}{4}(B'' - B')$.

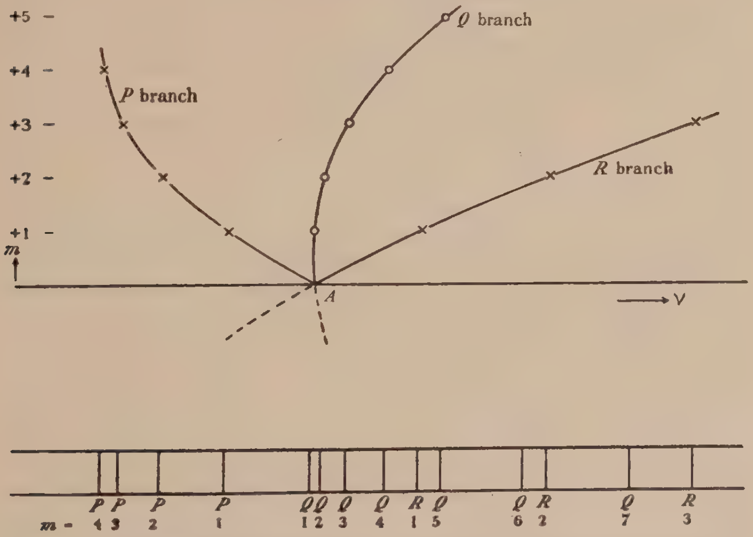

FIG. 27.—Schematic representation of the 5610 Å CO band, showing lines belonging to the P, Q, and R branches.

With m integral, equation (25) is in formal agreement with the empirical relation for the Q branch already mentioned.

The relationship to one another of the P, Q, and R branches of a band such as the CO emission band at 5610 Å, the internal structure of which appears to conform closely to (24) and (25), is shown schematically in Fig. 27. This is a band which degrades towards the violet, that is $(B'' - B')$ is positive. The head of the band is not actually included in the diagram—it is contained in the P branch for higher values of m. The common point of all three branches is A, but since this point corresponds to $m = 0$ both in equation (24) and in (25), it should not mark the position of a predicted line in any of the three series. However, the first predicted line of the Q branch ($m = 1$) actually coincides in frequency with that of the line at A which is forbidden by the restriction $m \neq 0$. This fact is also obvious from equation (25) which gives the same value of ν for $m = 0$ (forbidden) and $m = 1$ (allowed). It should be emphasised that the vertex of the Q parabola occurs, not at A, but at $m = \frac{1}{2}$, where, of course, there is no predicted line. The true origin of the band, defined as the frequency which would be emitted or absorbed if the molecule in the rotationless state underwent the electronic and vibrational change $(n'', p'') \rightarrow (n', p')$, is represented by A with frequency $\nu = \nu_{np}$. In the absence of a Q branch, this is the position of the " missing " line—$m = 0$ in equation (24).

The formulæ which we have derived above, while reproducing the main features of the simplest types of bands, are by no means of general validity. It should be noted that in deducing (24) and (25) we have ignored completely the corrections which would be required to take account of the variation of the moment of inertia of the molecule with rotation, as well as the mutual effects of vibration and rotation upon one another. It is probably due to these effects that additional terms (usually small) in m^3 and m^4 appear in the exact empirical equations for the P, Q, and R branches of the band. Again, we have assumed throughout that the rotational quantum number m is integral, but this is only likely to be true when the molecule does not possess any intrinsic angular momentum (due to electron spin) about the axis of rotation. It is the total resultant angular momentum of the molecule about this axis rather than that due solely to the nuclear rotation which requires to be quantised. By taking account of this, the frequent necessity for the use of half-integral values of m in equations (24) and (25) may be interpreted. Finally, we may mention that while the relation $E_m = \frac{h^2}{8\pi^2 I} m(m + 1)$ appears to hold (in the absence of electronic angular momentum) with $m = 0, 1, 2, 3,$ etc. for the energy of rotation of the diatomic heteropolar molecule, some further limitation of the possible values of m appears to be necessary in the case of the homopolar molecule. So far as is known at present, the observed structure of the electronic bands of such molecules as those of helium and hydrogen are best explained by restricting the values of m to odd integers. Some theoretical justification for this restriction in terms of the Schrödinger wave mechanics has recently been suggested by Dennison (*Nature*, **119**, 316, 1927).

Structure of the Band Group.—The origin or centre of the electronic band which arises from the transition $(n'', p'') \rightarrow (n', p')$ in emission or from the reverse transition in absorption has the frequency

$$\nu = \nu_n + (p'' + \tfrac{1}{2})\nu_v''\{1 - (p'' + \tfrac{1}{2})x''\} \\ - (p' + \tfrac{1}{2})\nu_v'\{1 - (p' + \tfrac{1}{2})x'\} \quad (26)$$

Multiplying out, this may be written in the form

$$\nu = \nu_0 - \beta' p' + \beta'' p'' + \gamma' p'^2 - \gamma'' p''^2 \quad . \quad . \quad (27)$$

$$\left.\begin{array}{ll}\text{where} & \beta' = \nu_v'(1 - x')\,;\ \beta'' = \nu_v''(1 - x'') \\ & \gamma' = \nu_v'x'\,;\ \gamma'' = \nu_v''x'' \\ \text{and} & \nu_0 = \nu_n + \tfrac{1}{2}\nu_v''(1 - \tfrac{1}{2}x'') - \tfrac{1}{2}\nu_v'(1 - \tfrac{1}{2}x')\end{array}\right\} \quad . \quad . \quad (28)$$

Since x' and x'' are both positive and small compared with unity, the coefficients β', β'', γ', and γ'' are always positive. Keeping to the same electronic jump in the molecule, ν_n, ν_v', ν_v'', x', and x'' are all constant, hence ν_0, β', β'', γ', and γ'' are also constants and p', p'' are the only variables on the right side of equation (27). This equation then gives the frequencies of the whole system of bands which are due to the various vibrational transitions which can be associated with one and the same electronic transition.

The expression agrees formally with the empirical equation (28) of Chapter I. to which the observed heads or centres of the bands of any group conform. From its theoretical derivation, we can immediately trace the origin of the Deslandres progressions and sequences into which the group sub-divides in practice. If we keep (in emission) to the same initial state of vibration (p'' constant) and vary the final state of vibration of the molecule, equation (27) reduces to

$$\nu = \nu_0' - \beta'p' + \gamma'p'^2\ (p' = 0, 1, 2, 3\ \ldots). \quad . \quad (29)$$

Since β' and γ' are both positive quantities, and γ' must normally be much smaller than β', this represents a series of lines which starts from the position $\nu = \nu_0'$ and proceeds in the direction of *increasing wave-length.* In this direction consecutive lines correspond to p', $p' + 1$, $p' + 2$, etc., and the separation of consecutive lines is given by

$$\Delta'\nu = \nu(p') - \nu(p' + 1) = \beta' - \gamma'(2p' + 1) \quad . \quad (30)$$

i.e. the separations form a converging arithmetical progression in the direction of increasing wave-length. These are, however, the characteristics of a *Deslandres first progression*, so that all the bands belonging to a progression of this type derive—in emission—from a common initial state of vibration of the excited molecule. Obviously, depending upon which particular state of vibration this may happen to be, we can have a considerable number of first progressions within the same main band group which will differ only in respect of the value of the constant ν_0'. Obviously, too, a Deslandres first progression in absorption must be interpreted to derive from transitions from various initial states of vibration of the absorbing molecule to one and the same final condition of the excited molecule.

On the other hand, if we pass (in emission) from a variable state of vibration of the excited molecule to a fixed state of vibration in its lower energy level (p' constant), the possible emission frequencies are given by

$$\nu = \nu_0'' + \beta''p'' - \gamma''p''^2\ (p'' = 0, 1, 2, 3\ \ldots)\ . \quad . \quad (31)$$

Having regard for the relative values of the coefficients β'' and γ'', these constitute a series of bands which start from the origin $\nu = \nu_0''$

and proceed therefrom in the direction of *increasing frequency*, converging as they do so. The separation of consecutive bands is

$$\Delta''\nu = \nu(p''+1) - \nu(p'') = \beta'' - \gamma''(2p''+1) \quad . \quad (32)$$

that is, the separations form a converging arithmetical progression in the direction of increasing frequency. Such a series of bands form a *Deslandres second progression*, which type of progression is therefore characteristic, whether in emission or in absorption, of a fixed vibrational state of the molecule in the lower of its two combining energy levels. The distinction between first and second progressions is made clear by reference to Fig. 10, which can now be regarded as a vibrational energy diagram of the molecule in two of its states of electronic excitation. The various possible states of vibration which can accompany the same electronic excitation result in a sub-division of each main level as shown. The convergence of the sub-levels in either group with increasing p' or p'' is a consequence of the anharmonic nature of the vibration—the factor which introduces the x's and y's into our equations. Were the vibration simple harmonic, the sub-levels would of course be equally spaced.

Finally each *sequence* of band heads results from transitions in which the vibration quantum numbers p'' and p' of the initial and final states differ by a fixed amount. We have different sequences for $p''-p'=0, p''-p'=1, p''-p'=-1, p''-p'=2$, etc. Putting $p''-p'=$ a constant in equation (27), it is easily seen that the frequencies of the bands in any one sequence can be expressed as a quadratic function either of p'' or of p', hence the separations of consecutive members of the sequence once again follow the arithmetical progression rule. The sequence converges towards the violet or towards the red depending upon whether γ'' is greater or less than γ'.

Arguing from the formal agreement of (27) with the empirical equation for the frequencies of the heads or centres of the totality of bands in a group, it might at first sight appear legitimate to equate the coefficients ν_0, β', etc. of (27) to the corresponding coefficients in the empirical equation and hence proceed directly to deduce the values of the molecular constants ν_n, ν_v', etc. by means of (28). Such identification of an empirical with our theoretical equation is only permissible, however, if the arbitrarily chosen integral variables p' and p'' of the former happen to be exactly equal to the true vibration quantum numbers of the latter. A moment's consideration will show that if the experimentally observed positions of the bands are capable of expression in the form

$$\nu = \nu_0 - \beta' p' + \beta'' p'' + \gamma' p'^2 - \gamma'' p''^2,$$

where p' and p'' are integral variables, they are equally capable of expression by *the same type of function* of any other integral variables p_1' and p_1'', where $p_1' = p' + a_1$ and $p_1'' = p'' + b_1$ and a_1 and b_1 are any integral constants. The new expression for the experimental frequencies would be

$$\nu = \nu_1 - \beta_1' p_1' + \beta_1'' p_1'' + \gamma' p_1'^2 - \gamma'' p_1''^2,$$

the γ's being the same as in the old expression, but the ν_1, β_1', and β_1'' different from ν_0, β', and β''. Actually, in his original systemisation of the bands of any group into progressions, Deslandres (through a natural misconception of which particular band marks the origin of the progression) used integral variables n and p which are now known to be related to the actual vibrational quantum numbers p' and p'' by the equations $p' = a - \mathrm{n}$, $p'' = b - \mathrm{p}$, where a and b are fairly large positive integers. It is clear, then, that some further guide is required to the actual relationship between the arbitrary integral variables of the empirical band group formula and the true quantum variables, before the molecular constants ν_n, ν_v', ν_v'', etc. can be evaluated.

Assignment of Vibration Quantum Numbers.—The only direct method of fixing the absolute values of the vibrational quantum numbers involved in an electronic band is, unfortunately, of limited applicability, depending as it does upon the measurement of the vibrational isotope effect, that is, the natural resolution of what should be a simple band into two components which occurs when one of the atoms in the molecule has two isotopic forms. While we cannot enter here into the details of the theory of this effect, we may note that the band constants ν_n, ν_v', ν_v'', etc. depend not only upon the chemical nature of the molecule, but also upon the masses of its constituent atoms. If we have two molecules A_1B and A_2B where A_1 and A_2 are isotopes, these two molecules will exhibit band spectra which agree in all essentials of general structure, but differ slightly in the spectral positions of corresponding bands. The computed isotope displacement is not a constant for all bands of the same group, however, but depends upon the absolute values of p' and p'', and so from observation of the displacement of any band the true vibration quantum numbers concerned can be decided upon. It was from observation of the isotope effect in the emission bands of boron monoxide that Mulliken was led to the presumption that this molecule must possess a finite amount $\frac{1}{2}h\nu_v$ of permanent or residual energy of vibration (zero-point energy), a result which foreshadowed the implication of the modern wave mechanics that the energy of vibration of the simple harmonic oscillator is not $ph\nu_v$ but $(p + \frac{1}{2})h\nu_v$.

Failing the use of the above method, a plausible assignment of vibration quantum numbers to the different bands of a group can still be effected once the group is resolved into progressions and sequences. For each main electronic energy level of the molecule, the spacing between successive vibrational sub-levels decreases regularly with increasing vibration quantum number—a fact which leads to the spacing rules for first and second progressions already formulated. In addition to this, however, the intensities of the successive bands in any progression must also be expected to be regularly graded, and all bands which derive from the same initial level should exhibit the same perturbations. Having picked out the members of any one progression, the *relative* values of the p's for the variable sub-levels involved are then easily settled, and their *absolute* values can often be decided on the general principle that the largest value of $\Delta'\nu$ in any first progression corresponds to the spacing between the levels for which $p' = 0$ and $p' = 1$. The same procedure naturally applies to second progressions. Again, the most probable initial state, whether in emission or in absorption, is usually the vibrationless state of the molecule, and bands deriving from this state are therefore the most intense in the group. In particular, the band corresponding to the transition $p'' = 0 \rightarrow p' = 0$ in emission or $p' = 0 \rightarrow p'' = 0$ in absorption is often the most prominent. If this one band can be identified, the quantum parameters of all the other bands follow. Another criterion of the position of this central band is the successive shortening of the sequences which takes place beyond this position. A glance at Fig. 28 which illustrates the second positive group of nitrogen (with the correct assignment of quantum numbers) shows that, moving from left to right, the sequence $p'' - p' = 0$ which includes the band $0 \rightarrow 0$ is the last to possess a normal number of constituents. The following sequences $p'' - p' = 1$, $p'' - p' = 2$, etc. lack one, two, etc. members respectively. This shortening is often a very obvious phenomenon, since the first member of each normal sequence is usually the strongest band of the sequence, and it is the strongest band of the sequence which suddenly disappears when we pass beyond the true centre of the group.

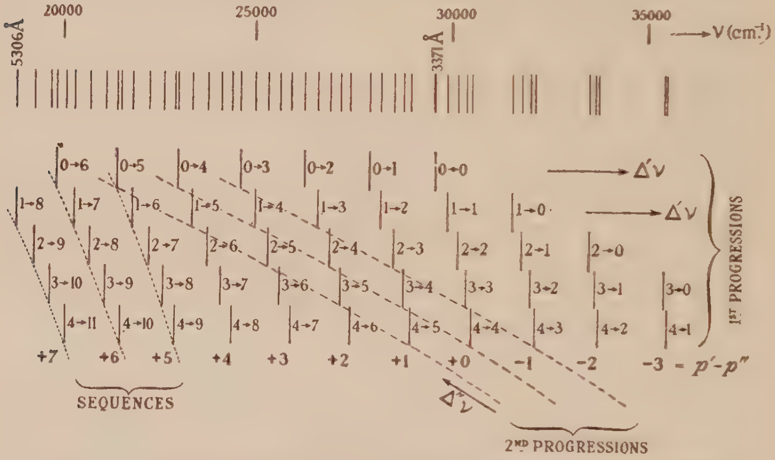

FIG. 28.—Second positive group of nitrogen. Band heads arranged in progressions and sequences.

The Second Positive Group of Nitrogen.—Figs. 10 and 28 represent two different methods of showing diagrammatically the regularities of the progressions and sequences of a band group in terms of the vibrational energy levels involved. The same regularities are expressed quantitatively by tabulating the wave-numbers of the bands as in Table XVIII., which refers again to the second positive group of nitrogen in emission. Here each horizontal row of wave-numbers represents a Deslandres first progression, each vertical row a second progression. The wave-numbers of the bands which form a sequence lie on a diagonal. The spacings $\Delta'\nu$ and $\Delta''\nu$ of consecutive bands in the different progressions are given by the numbers in parentheses. These spacings have the following meaning. The spacing $\Delta'\nu_{2\frac{1}{2}}$ of the two consecutive bands which have a common value of p'' and the values 2 and 3 for p' is a measure of the distance between the sub-levels $p' = 2$ and $p' = 3$ of the molecule in its lower electronic state. The value of $\Delta'\nu_{2\frac{1}{2}}$ obtained from each first progression should therefore be a constant, as is borne out by the column of values of $\Delta'\nu_{2\frac{1}{2}}$ in parentheses. This spacing is not, however, equal to $\Delta'\nu_{1\frac{1}{2}}$ or $\Delta'\nu_{3\frac{1}{2}}$. Actually the consecutive spacings $\Delta'\nu_{\frac{1}{2}}$, $\Delta'\nu_{1\frac{1}{2}}$, $\Delta'\nu_{2\frac{1}{2}}$, etc., when multiplied by h, represent the magnitudes of the successive quanta of vibrational energy which the molecule in its lower state of electronic excitation may acquire. Corresponding to the anharmonic nature of the vibration, these energy quanta should fall off in value with increasing p', and in conformity with equation (30) if the anharmonic character of the vibration is sufficiently taken account of by the first power correction term of (20a). In agreement with this, the averaged values of $\Delta'\nu$ in the last row of the table form a decreasing arithmetical progression to a close approximation. On the other hand, each $\Delta''\nu$ is a measure of the difference between consecutive vibration levels of the molecule in its upper state of electronic excitation, and the successive $\Delta''\nu$'s thus represent the magnitudes of the successive vibration quanta which the molecule in this state may acquire. These energy quanta also fall off in value with increasing vibration quantum number p'' (cf. last column of table), but not in such good accord with the predicted behaviour of equation (32). While the plot of $\Delta'\nu$ against p' is a straight line, that of $\Delta''\nu$ against p'' curves over towards the p'' axis. This point will be reverted to later.

From the data of Table XVIII. it is now possible to compute certain of the characteristics of the nitrogen molecule in the two states of electronic excitation which are involved in the emission of these bands. The wave-number of the origin of the group, that is, of the band emitted in the transition $(n'' \rightarrow n'; \ p'' = 0 \rightarrow p' = 0)$ is $\nu_0 = 29{,}666$ cm.$^{-1}$. Expressed in energy terms this means that the one level of electronic excitation is about 84,000 calories or 3·66 volts above the other. However, neither of these levels, as we shall see, represents the normal nitrogen molecule. Again, from equation (30), the first and second $\Delta'\nu$'s of the last row of the table should equal $\beta' - \gamma'$ and $\beta' - 3\gamma'$ respectively, whence $\beta' = 1718$ cm.$^{-1}$ and $\gamma' = 14$ cm.$^{-1}$. It follows from (28) that $\nu_v' = 1732$ cm.$^{-1}$ and $x' = 8{\cdot}1 \times 10^{-3}$. The *first* vibration quantum acquired by the molecule in the lower electronic state is equivalent to $\Delta'\nu_{\frac{1}{2}} = \beta' - \gamma' = 1704$ cm.$^{-1}$, which in energy units works out to be 4850 calories per mole or 0·21 volt. Again,

TABLE XVIII.

Deslandres First and Second Progressions in Second Positive Group of Nitrogen.

(Wave-numbers of band heads.)

p' → p'' ↓	0	$\Delta'\nu_{\frac{1}{2}}$	1	$\Delta'\nu_{1\frac{1}{2}}$	2	$\Delta'\nu_{2\frac{1}{2}}$	3	$\Delta'\nu_{3\frac{1}{2}}$	4	$\Delta'\nu_{4\frac{1}{2}}$	5	$\Delta'\nu_{5\frac{1}{2}}$	6	Average $\Delta''\nu$
0	29666·4	(1702·8)	27963·6	(1676·4)	26287·2	(1649·8)	24637·4	(1612·7)	23024·7	(1589·5)	21435·2	(1557·6)	19877·6	↓
$\Delta''\nu_{\frac{1}{2}}$	(1996·4)		(1993·3)		(1995·9)		(1997·6)		(1997·0)		(1990·4)		(1990·9)	(1994·5)
1	31662·8	(1705·9)	29956·9	(1673·8)	28283·1	(1648·1)	26635·0	(1623·3)	25011·7	(1586·1)	23425·6	(1557·1)	21868·5	
$\Delta''\nu_{1\frac{1}{2}}$	(1939·2)		(1942·1)		(1939·9)		(1944·1)		(1947·0)		(1945·8)		(1939·5)	(1942·5)
2	33602·0	(1703·0)	31899·0	(1676·0)	30223·0	(1643·9)	28579·1	(1620·4)	26958·7	(1587·3)	25371·4	(1563·4)	23808·0	
$\Delta''\nu_{2\frac{1}{2}}$	(1875·2)		(1873·3)		(1871·6)		(1870·1)		(1875·0)		(1873·0)		(1875·7)	(1873·4)
3	35477·2	(1704·9)	33772·3	(1677·7)	32094·6	(1645·4)	30449·2	(1615·5)	28833·7	(1589·3)	27244·4	(1560·7)	25683·7	
$\Delta''\nu_{3\frac{1}{2}}$	(—)		(1775·6)		(1776·1)		(1775·5)		(1774·0)		(1780·3)		(1782·7)	(1777·4)
4	—	(—)	35547·9	(1677·2)	33870·7	(1646·0)	32224·7	(1617·0)	30607·7	(1583·0)	29024·7	(1558·3)	27466·4	
Average $\Delta'\nu$ →		(1704·1)		(1676·2)		(1646·6)		(1617·9)		(1587·0)		(1559·4)		

by equating the first and second $\Delta''\nu$'s of the last column of the table to $\beta'' - \gamma''$ and $\beta'' - 3\gamma''$ respectively, we obtain $\beta'' = 2020$ cm.$^{-1}$ and $\gamma'' = 26$ cm.$^{-1}$, whence $\nu_v'' = 2046$ cm.$^{-1}$ and $x'' = 12{\cdot}7 \times 10^{-3}$. The first vibration quantum in the higher electronic state is now 5670 calories per mole or 0·245 volt. This first vibration quantum is in each case a measure of the strength of binding of the two atoms in the vibrationless ($p = 0$) molecule, so that the chemical bond is in the present instance stronger when the molecule is in the higher of the two electronic levels. That this should be so is by no means general, of course, but its truth in the present instance is independently attested by the values of the moments of inertia I' and I'' of the molecule in the two states in question. The fact that all the bands of the second positive group of nitrogen degrade towards the violet means that $I' > I''$ (cf. p. 192). The actual values as computed from the detailed structure of any band of the group are $I' = 16{\cdot}98 \times 10^{-40}$ and $I'' = 15{\cdot}24 \times 10^{-40}$ c.g.s. units. Naturally, the stronger the binding, the closer the two atoms will be to one another in the molecule and therefore the smaller will be its moment of inertia. This is one illustration of the general rule that, for the same molecule, an increase in the initial spacing of the vibrational sub-levels for a change in electronic level is invariably associated with a decrease in I and *vice versa*.

The Electronic Energy Levels of the Nitrogen Molecule.—It will be instructive now to consider briefly the general features of the other groups of bands associated with the nitrogen molecule and their relationship to the group which has just been dealt with. These other groups are termed the "first positive," the "fourth positive," and the "ultra-violet." The first and fourth, like the second positive group, are only observed in emission, but the "ultra-violet" group occurs both in emission and in absorption, and for this reason is believed to be the resonance spectrum of the nitrogen molecule, involving the normal state of the molecule as the lower of the two combining states. The table below contains the characteristics of all four groups as given by Birge (*Bull. Nat. Research Council*, **11,** 232, 1926).

TABLE XIX.

BAND GROUPS OF NITROGEN (UNIONISED).

Group.	Spectral Region ($\mu\mu$).	Direction of Shading of Bands.	ν_0 (cm^{-1}).	ν_0 in volts.	β''.	γ''.	β'.	γ'.
First positive	900-500	Violet	10979	1·36	1718·4	14·44	1474·4	13·98
Second positive	550-270	,,	29653	3·66	2018·7	26·05	1718·4	14·44
Fourth positive	290-230	,,	44218	5·45	—	—	1718·4	14·44
Ultra-violet	185-120	Red	68957	8·51	1679·2	13·85	2345·2	14·45

From the identity of the β''s and γ''s of the second and fourth positive groups with the β'' and γ'' of the first positive group, it follows that the second and fourth groups have a common *final* electronic level which is also the *initial* level for the first group. On the other hand, neither of the two electronic levels involved in the emission or absorption of the ultra-violet group can be identified with the other electronic levels. Apparently, then, the four groups of bands involve six distinct electronic energy levels of the molecule, including the ground level of the normal molecule. These are represented diagrammatically in Fig. 29 where the known vibrational sub-levels of each main electronic level are also indicated. The origins of the different band groups are as follows :—

Ultra-violet Group : $A' \rightleftharpoons X$. Observed combinations in absorption: $p_X = 0$ with $p_{A'} = 0, 1, 2, 3, 4 \ldots 10$. Observed combinations in emission : $p_X = 0, 1, 2, \ldots 11$ with $p_{A'} = 0, 1, 2$, and 3.

First Positive Group : $B \rightarrow A$. Emission only. Observed combinations are $p_A = 0, 1, 2 \ldots 16$ with $p_B = 0, 1, 2, \ldots 20$.

Second Positive Group : $C \rightarrow B$. Emission only. Observed combinations are $p_B = 0, 1, 2 \ldots 11$ with $p_C = 0, 1, 2, 3, 4$.

Fourth Positive Group : $D \rightarrow B$. Emission only. Observed combinations are $p_B = 0, 1, 2 \ldots 6$ with $p_D = 0$.

An ultra-violet group of bands corresponding to the combination $A \rightleftharpoons X$ has been sought for, by Birge and Hopfield in emission, and by Sponer in absorption, but no evidence of its existence was obtained, from which it has been suggested that state A, which is the final state of the molecule in the emission of the first positive group, is metastable in the same sense as is the 2^3P_0 state of mercury. The spectral position of this predicted group would be approximately that of the ultra-violet group $A' - X$ which is actually observed, but the external characteristics of the level A' definitely preclude its identification with A (cf. Table XIX.).

The position of the excitation level A' relative to the normal level X, and also the positions of levels B, C, and D relative to A can easily be deduced from the spectroscopic data, since the ν_0 of any group of bands, when expressed in energy units, represents the difference between the energy contents of the molecule in the two states of electronic excitation concerned. These differences are given in volts in the fifth column of Table XIX. From them we see that level A', which is attained by the ultra-violet absorption of the normal nitrogen molecule, is 8·51 volts above X, while the spacings A—B, B—C, and C—D are 1·36, 3·66, and 1·79 volts respectively. Since no band group is known, however, connecting any of the levels A, B, C, D with X, it is necessary to appeal to evidence other than spectroscopic in order to find these levels relative to X.

A large number of excitation potentials of doubtful significance from 6·3 volts upwards have been obtained for molecular nitrogen by the method of electronic impact. On various counts, the potential which seems least doubtful as regards its interpretation is probably that of 13·0 ± 0·3 volts obtained by Sponer (*Z. Physik*, **34,** 622, 1925)

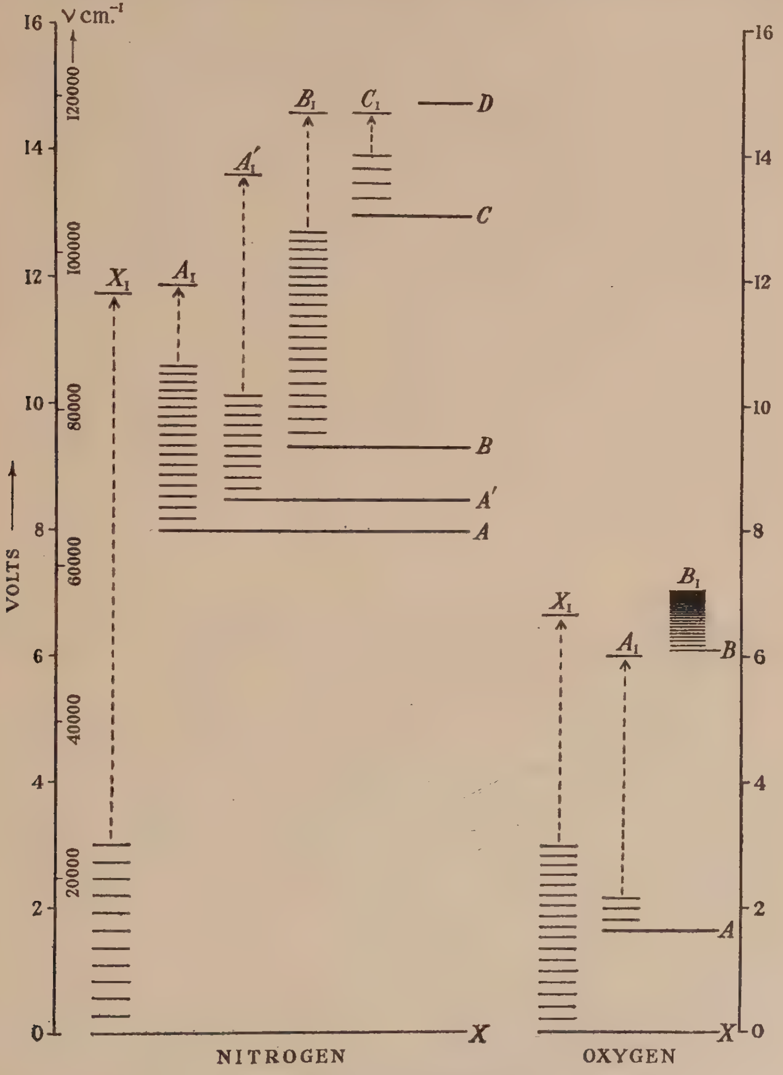

FIG. 29.—Energy levels of nitrogen and of oxygen.

as the minimum potential required for the excitation of the zero band of the second positive group. This means that level *C* is 13 volts above the ground level *X*, hence the separation of *A* and *X* is 8 volts. The energy levels of Fig. 29 are drawn on this basis.

THE VIBRATIONAL SUB-LEVELS OF THE MOLECULE AND THEIR CONVERGENCE LIMITS.*

Nitrogen.—In the energy diagram of Fig. 29, the known vibrational sub-levels attached to each electronic level of the nitrogen molecule are also indicated. As already pointed out, the actual spacing of these vibrational energy levels can be obtained directly from the frequency differences $\Delta\nu_{\frac{1}{2}}$, $\Delta\nu_{1\frac{1}{2}}$, $\Delta\nu_{2\frac{1}{2}}$ . . . of the consecutive bands in the pertinent Deslandres progression by merely converting these frequency differences into energy units. If the Deslandres progression of bands is accurately described by an equation of the form (29) or (31), these frequency differences and hence the sub-level spacings will form a decreasing arithmetical series, in other words, the plot of $\Delta\nu$ against the vibration quantum number p will be linear. This is very nearly true for the sub-levels attached to the electronic levels X, A', A, and B of the nitrogen molecule, as is shown by the plots of $\Delta\nu$ against p in Fig. 30, but not for the sub-levels attached to C which converge much more rapidly than would correspond to the arithmetical progression law. The pronounced curvature of the line C as compared with the practical linearity of X, A', A, and B means that the anharmonic nature of the molecule's vibration when in the electronic state C is not sufficiently taken account of by the first power term in x in our general expression for the energy of vibration :—

$$E_p = (p + \tfrac{1}{2})h\nu_v\{1 - (p + \tfrac{1}{2})x - \;.\;.\;.\}.$$

It is this first power term in x which introduces the γp^2 term into the progression law (29) or (31). Further significant terms in x^2, x^3, etc. would introduce additional terms in p^3, p^4, etc. in (29) or (31).

In the energy diagram (Fig. 29) it will be noted that the known vibrational sub-levels have been extrapolated in each case to the position of zero spacing of consecutive sub-levels. This extrapolation is in practice effected graphically by continuing the pertinent curve of $\Delta\nu : p$ of Fig. 30 till it meets the p axis. Taking curve B as example, this is produced till it meets the p axis at say p_0, at which point $\Delta\nu$ becomes zero. The area enclosed between the full curve and the co-ordinate axes is

$$\sum_0^{p_0} \Delta\nu \text{ or } \int_0^{p_0} \Delta\nu \, . \, dp,$$

where $\Delta\nu$ is expressed analytically as a continuous function of p, and this quantity, when expressed in energy units by multiplying by hc, gives the distance of the convergence limit of the sub-levels of B above the electronic level B itself.

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* The subject matter of this section is derived chiefly from an important paper by Birge and Sponer (*Phys. Rev.*, **28**, 259, 1926) entitled " The Heat of Dissociation of Non-Polar Molecules."

Ignoring for the moment any question as to the legitimacy of such extrapolation, the meaning of the so obtained convergence limit would be as follows. To the molecule originally in the electronic state B we give successive quanta of vibrational energy. The vibration of the moving parts in the molecule is by hypothesis anharmonic in character (were it not so, the known sub-levels would of course be equally spaced), hence the mean linear separation of the vibrating parts increases progressively as the vibrational energy is increased. Simultaneously the chemical binding of the parts is weakened and the natural frequency of vibration, which governs the magnitude of the next added vibration quantum, decreases. When this falls to zero the binding force is zero and the vibrating parts are completely separated from one another, that is, the molecule is dissociated. Accordingly we have in the distance BB_1 separating the convergence limit of the vibrational sub-levels from their parent electronic level a measure of the heat of dissociation of the molecule into its component parts. This heat of dissociation, however, requires careful definition. The ordinary heat of dissociation of the diatomic molecule is the amount of energy required to separate the *normal* molecule into two *normal* atoms. The distance BB_1 however measures, not the energy required to dissociate the normal molecule, but rather that required to dissociate the molecule which has previously been excited to the state B. Since the initial excitation of this molecule is XB, it is the total distance XB_1 which measures the heat of dissociation of the normal molecule into resultants. Again, these resultants cannot be two normal nitrogen atoms since it would seem physically impossible to pass adiabatically from an excited electronic configuration of the homopolar molecule to the system of two normal atoms. If one of the resultants is a normal atom, the other must be an excited atom N* with one of its valency electrons (the optical electron of the parent

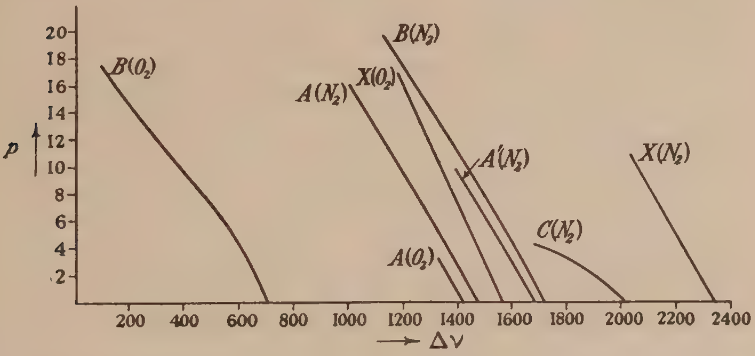

FIG. 30.—Plots of $\Delta\nu$ against p for various electronic states of nitrogen and of oxygen.

molecule) displaced to some outer orbit. The dissociation process is then represented by

$$N_2 \text{ (normal)} + BX_1 \text{ volts} \rightarrow N + N^*.$$

Since we have no means of foretelling exactly how much internal energy this excited atom will have, it is clearly impossible to infer from the magnitude of BX_1 what the true energy of dissociation of the molecule is. The same difficulty of interpretation is encountered with regard to the convergence limits A_1, A_1', and C_1. All that we can say is that, if the products of dissociation are in each case a normal and an excited atom, then the convergence limits A_1, A_1', B_1, and C_1 should give the relative spacings of different energy levels of the nitrogen atom.

A simpler meaning attaches to the extrapolated convergence limit X_1 of the vibrational sub-levels of the normal state X of nitrogen. If we start with the normal non-vibrating molecule and gradually increase its vibrational energy content, we would expect to finish with two normal atoms as the products of dissociation. Accordingly XX_1 should represent the true heat of dissociation of nitrogen as above defined. From the data of the "ultra-violet" band group of nitrogen, Birge and Sponer (cf. Sponer, *Proc. Nat. Acad. Sci.*, **13**, 100, 1927) have effected the necessary extrapolation of the vibrational sub-levels of X and find that XX_1 is about 11·75 volts. This corresponds to a heat of dissociation D_{N_2} of 271,000 calories. Such a high value for D_{N_2} is in accord with the chemical inertness of the molecule, but no thermochemical data are available from which D_{N_2} might be directly obtained. However, Sponer (*Z. Physik*, **34**, 622, 1925) from a consideration of the after-glow of "active nitrogen" has arrived at an indirect value for D_{N_2} which is in substantial agreement with the above figure. The strongest bands observed in the after-glow of active nitrogen belong to the first positive group and correspond to transitions of the emitting molecule from the sub-level $p = 11$ of electronic level B to different sub-levels of A (cf. Fig. 29). Sponer, by assuming that active nitrogen is atomic nitrogen, infers that the energy of this level (i.e. its height above level X) measures the true heat of dissociation of nitrogen. This energy is 11·4 volts and is taken by Birge and Sponer as a fairly correct estimate of D_{N_2}. It will be realised, of course, that a more exact agreement of these two estimates of D_{N_2} is hardly to be expected, since on the one hand the value $D_{N_2} = 11{\cdot}75$ volts depends upon a not too certain extrapolation of the sub-levels of X, while on the other hand the value $D_{N_2} = 11{\cdot}4$ volts depends on Sponer's value of 13 volts for the excitation potential of level C, an experimental observation (cf. p. 203) which is only likely to be correct within a few tenths of a volt. Birge has recently extrapolated the sub-levels of A' to a convergence limit A_1' which lies 5·15 volts above A' or 13·65 volts above the normal level X of the molecule. Assuming that the products of the hypothetical dissociation to which this convergence limit would correspond are one normal and one excited nitrogen atom, and using Sponer's value of 11·4 volts for the true heat of dissociation of the molecule, the resultant excited nitrogen atom should have 2·25 volts excess energy. It is possibly significant that the atom of nitrogen does possess an excitation level fairly close to this, actually 2·4 volts above the normal.

Oxygen.—Another interesting case considered by Birge and Sponer is that of oxygen. Two main electronic energy levels of this molecule besides the normal are known from band spectra data. The one A lies 1·62 volts, the other B lies 6·1 volts above the normal level X. Sub-levels of X up to $p = 17$ are found in the Runge emission bands of oxygen. These sub-levels converge slowly but regularly as in the case of the X sub-levels of nitrogen, and their extrapolated convergence limit (at $p = 69$) lies at 6·65 volts. In calories this is 153,000 and, if the extrapolation is correct, it should represent the true heat of dissociation of oxygen. Only the first few sub-levels attached to A are known. These are widely spaced and any attempt to extrapolate to a convergence limit would be of doubtful significance. As regards the sub-levels of B, these are very closely spaced (cf. Fig. 29), and they present an interesting feature not encountered with nitrogen in that their convergence limit B_1 is realised experimentally. This results from the peculiar character of the ultra-violet absorption spectrum of oxygen. This spectrum consists of a rapidly converging progression of bands for each of which the absorbing molecule starts from the zero level X and goes to some sub-level of B. The separate bands can be identified up to $p_B = 18$; beyond this they obviously coalesce to a convergence limit, but the exact position of this is obscured owing to the fact that an extended region of strong continuous absorption begins there and stretches further into the ultra-violet. However, to obtain the convergence limit of the bands, it is only necessary to carry out a short and entirely justifiable extrapolation from the last resolved band, which is No. 18 of the progression, to No. 21. The convergence limit of the progression so obtained lies at 1751 Å, only five Ångstrom units beyond the last measured band, and its frequency, when expressed in energy units, obviously gives the distance of B_1 above the zero level of energy X of the molecule. This works out to be 7·05 ± 0·01 volts. The absorption spectrum of oxygen is clearly to be interpreted in the sense that absorption of the convergence frequency itself by the normal molecule is just sufficient to dissociate it into its components; absorption of any frequency in the region of continuous absorption beyond the convergence frequency also effects the dissociation, the excess energy appearing in the resultants as energy of free translatory motion which is not quantised. The value of 7·05 volts thus derived for the energy of "optical" dissociation of the oxygen molecule is not necessarily equal to the true heat of dissociation, since, by the mode of splitting the molecule under consideration, at least one of the resultant atoms must find itself in an internal energy level above the normal. As in the case of the convergence limit to level B of nitrogen, we cannot definitely specify what these dissociation products are, but fortunately this does not prevent us in the present instance from forming a fairly accurate estimate of the true heat of dissociation of oxygen. The first energy levels of the oxygen atom above the normal (derived from the arc spectrum of the oxygen atom) occur at 0·02 and 0·03 volt. The next level represents 9·1 volts of energy of excitation. It is clearly impossible that either of the oxygen atoms resulting from the optical dissociation should possess 9·1 volts excess energy, hence the possible internal energy content of each resultant atom is restricted to zero, 0·02 volt, or 0·03 volt. If both resultant atoms are normal, the true heat of dissociation is $D = 7{\cdot}05$ volts. If one resultant atom is normal and the other excited, the least possible value of D is 7·02 volts. If both resultant atoms are excited, the least possible value of D is 6·99 volts. It would seem that we are certainly justified in assuming that D is 7·02 ± 0·05 volts. Expressed in calories this becomes

$$D_{O_2} = 162{,}000 \pm 1000 \text{ calories.}$$

Birge and Sponer (*loc. cit.*) remark that this value of D_{O_2} checks well with the rough estimate of 162,000 made by Born and Gerlach (*Z. Physik*, **5,** 433, 1921) from the observed long wave-length limit of the the photochemical formation of ozone from oxygen (see, however, Chapter VIII).

It will be noted that the value 7·02 volts is appreciably higher than the first estimate of D (6·65 volts) obtained from the extrapolated convergence limit of the vibrational sub-levels of X. It must be remembered, however, that a rather extensive extrapolation from $p = 17$ to $p = 69$ has to be made in obtaining this convergence limit, and Birge and Sponer consider that the discrepancy of 0·4 volt between the two values of D may be regarded as an indication of the probable error of such extrapolation.

Hydrogen.—The heat of dissociation of the hydrogen molecule also can be computed from spectroscopic data alone. The complete emission spectrum associated with this molecule has now been analysed into several groups of bands, corresponding to which there appear to be about fifteen different possible states of electronic excitation of the molecule (cf. Birge, *Proc. Nat. Acad. Sci.*, **14,** 12, 1928). Of these, however, we shall be concerned only with the normal state, which as before we shall designate by X, and one excited state B which lies 11·1 volts above X. Now the emission spectrum in the far ultraviolet region between 165 and 100 $\mu\mu$ contains a large group of bands of open structure which can be arranged into five progressions corresponding to transitions of the excited molecule from various sub-levels of B to various sub-levels of X. This emission spectrum can be considerably simplified, as Lyman first observed, if the hydrogen in the discharge tube is mixed with argon. Under these conditions the emission consists solely of a single progression of bands—the "Lyman" bands—which all derive from one and the same vibrational sub-level of B. From an analysis of this simplified spectrum, Witmer (*Proc. Nat. Acad. Sci.*, **12,** 238, 1926) has obtained the spacings of the first eleven vibrational sub-levels of the normal state X of the molecule, and, by a short and reasonable extrapolation to their convergence limit, deduced a value for the heat of dissociation of hydrogen equal to 4·34 volts or 100,000 calories. According to Birge, this value is likely to be correct within 0·1 volt or 2000 calories. Other recent estimates of the heat of dissociation of hydrogen with which this may be compared are (1) $D = 101{,}400$ calories, obtained by Condon (*Proc. Nat. Acad. Sci.*, **13,** 466, 1927) from a theoretical consideration of the binding of the atoms in the molecule in terms of wave mechanics, (2) $D = 106{,}000 \pm 3000$ calories, calculated by Bodenstein and Jung (cf. p. 467) from the rate of formation of hydrogen bromide, and (3) $D = 105{,}000 \pm 3500$ calories, obtained by Bichowsky and Copeland (*J. Amer. Chem. Soc.*, **50,** 1315, 1928) by direct calorimetric measurement of the heat of association of atomic hydrogen. The average of these last three estimates is 104,000 calories, in good agreement with the spectroscopic value.

One or two questions arise out of the preceding discussion which must now be considered in more detail. In the first place we may enquire how far the practical extrapolation of the known vibrational sub-levels of any molecule to a convergence limit can be justified on theoretical grounds. To make the nature of the problem clear, we may recall that the vibrational sub-levels of the normal nitrogen molecule are known up to sub-level $p = 11$. At this point, however, the spacing $\Delta\nu$ of consecutive sub-levels has only fallen from the initial value of 2331 cm.$^{-1}$ to 2042 cm.$^{-1}$, so that the estimation of the convergence limit, at which $\Delta\nu = 0$, obviously entails a very extended extrapolation. It is true that in the case considered the observed spacings conform accurately to the linear relation

$$\Delta\nu = \beta - \gamma(2p + 1)$$

where $\beta = 2345{\cdot}2$ and $\gamma = 14{\cdot}45$, that is, the plot of the first eleven $\Delta\nu$'s against p is a straight line * (cf. curve X of Fig. 30). Nevertheless, unless we can justify the assumption that this regular decrement in the spacings will more or less continue right up to the convergence limit, the value of the heat of dissociation of the molecule which is computed on the basis of the extrapolation is open to serious criticism.

Some theoretical justification for assuming the practical persistence of the convergence law *in the case of non-polar molecules* has been obtained by Kratzer (*Z. Physik*, **26,** 40, 1925) from a consideration of the law of force governing the binding of the atoms in the molecule. Writing this law of force in the form of a series of powers of $1/r$, where

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* It seems indeed to be a rule of general applicability that the known $\Delta\nu$'s for the *normal* sub-levels of any molecule should decrease linearly with increasing p.

r is the nuclear separation, Kratzer distinguishes between two cases. (*a*) If the important term in the region of large values of r is the inverse square or the inverse cube power, he finds that the $\Delta\nu : p$ curve does not cut the p axis at any finite value of p, but approaches it asymptotically as in the full curve (*a*) of Fig. 31. The slope of the curve (*a*) may first decrease instead of continually increasing as shown, but if so a point of inflection is reached beyond which it turns upwards. The heat of dissociation of the molecule, which is proportional to the total area enclosed by the curve and the co-ordinate axes, is finite, that is, there is a limit to the value of the vibrational energy which the molecule can acquire, but there is no limit to the value of the vibration quantum number p. This should be the case for polar molecules which separate into two ions, since the law of force between the component ions is the inverse square law, at least for fairly large distances of separation. For such a molecule, then, even if the initial portion of the $\Delta\nu : p$ curve is known from band spectra data, the shape of the curve (*a*) shows that it should be impossible by extrapolation to estimate the heat of dissociation with any degree of certainty. (*b*) If the series expansion of the binding force for fairly large separation of the nuclei begins with an inverse fourth or higher power term in r, then, even though the curve may not be strictly linear but turn upwards, it intersects the p axis for a finite value of p (cf. full curve (*b*)). As before, the included area, which measures the heat of dissociation of the molecule, is finite, but so also is the limiting value of the vibration quantum number p. Now for a homopolar molecule the binding force at large nuclear separation is due mainly to polarisation effects, and the probable law of force for large separation is one involving a high inverse power of r such as the ninth. The predicted character of the $\Delta\nu : p$ curve for such a molecule should then be somewhat as shown by the full curve (*b*), and a

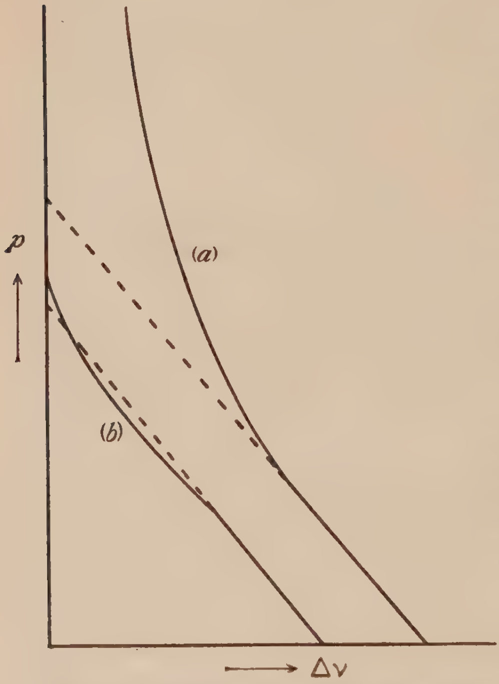

FIG. 31.—Theoretical shape of $\Delta\nu : p$ curve for (*a*) polar molecules, (*b*) non-polar molecules.

comparison of the area enclosed by the full curve (*b*) with that enclosed by the dotted curve which is a linear extension of the first portion shows that for homopolar molecules a linear extrapolation of the known vibrational sub-levels should give a fairly reasonable estimate of the heat of dissociation. The estimate is likely to be the closer, of course, the longer the initial range over which the observed $\Delta\nu : p$ curve is strictly linear. Finally, we may remark the general resemblance between the curve (*b*) and the experimental curve *B* of Fig. 30 for the *B* sub-levels of oxygen which happens to be almost complete.

THE OPTICAL DISSOCIATION OF HOMOPOLAR MOLECULES.

In the preceding Section, two different methods have been indicated by which the heats of dissociation of homopolar molecules may be computed from band spectra data. In the one method, the known vibrational sub-levels of the *normal* molecule are extrapolated to a convergence limit and the products which would result from this hypothetical increase in the vibrational energy of the molecule (which is not coupled with electronic excitation) are assumed to be the normal atoms. The other method uses the convergence limit of the known vibrational sub-levels of some *excited* state of the molecule, and works on the assumption that the resultants of the dissociation are again atoms, one or both of which, however, may possess some excess internal energy by virtue of the original electronic excitation of the molecule.

The probable accuracy of the result predicted by either method depends, as we have seen, on the length of the extrapolation which has to be carried out from the last known vibrational sub-level to the convergence limit in question. Of the three examples of homopolar molecules studied, oxygen is the only one for which a really accurate estimate of *D* has been effected, since for this case alone is a convergence limit to the vibrational sub-levels of one state of the molecule (state *B*) realised without the necessity for extrapolation. This happens because in the absorption spectrum of oxygen we have a converging progression of absorption bands, due to transitions of the molecule from the ground level *X* to different sub-levels of *B*, which actually persists right up to an optical convergence limit. This optical convergence limit of the discontinuous series of bands marks the beginning of a region of strong *continuous* absorption, which can only be interpreted to mean that for absorption within this region the change in vibrational energy which is coupled with the electronic transition in the molecule is more than sufficient to effect the complete separation of the vibrating parts. In other words, the oxygen molecule is dissociated by the elementary act of absorption at the convergence limit and also in the continuous region beyond.

One would expect the ultra-violet absorption spectrum of the normal nitrogen molecule to be essentially similar to that of oxygen, but although the progression of absorption bands observed by Sponer for nitrogen converge regularly, the absorption stops long before any convergence limit is reached, and further there is no region of continuous absorption starting at the extrapolated convergence limit of the observed bands. This difference in the absorption spectra of the two molecules may be alternatively expressed by saying that, whereas with oxygen a very large change in vibrational energy (sufficient or more than sufficient to cause dissociation) can accompany the transition which the electronic system of the molecule undergoes by absorption, with nitrogen the possible change in the vibrational energy coupled with the electronic transition is for some reason limited to less than is required to effect the dissociation.

That it is the magnitude of the vibrational energy change suffered by the molecule and not the total (vibrational + electronic) energy change which normally determines whether or not the act of absorption will cause dissociation is amply evidenced by the fact that practically any molecule can acquire much more electronic energy than corresponds to the heat of dissociation without dissociation actually taking place. One example often cited is provided by the iodine molecule which (when illuminated by the Hg line 1849 Å) can absorb and re-emit as fluorescence an amount of energy five times the heat of dissociation without dissociation taking place. Again, in the emission spectrum of the hydrogen molecule there are bands which show that the emitting molecule possesses four or five times as much energy of electronic excitation as would suffice to dissociate it were this energy otherwise located. A glance at the energy diagram of nitrogen (Fig. 29) shows that the molecules which emit the bands of the second positive group ($C \rightarrow B$) are all in such a condition that they possess considerably more energy than corresponds to their heat of dissociation. The bulk of the energy content is, however, in the form of electronic excitation (CX) and is not available for the purpose of splitting the molecule into atoms.

The possibility of primary dissociation of a molecule by absorption of radiation is a matter of particular interest to the worker in photochemistry, since for most "light" reactions the mechanism of reaction which is postulated must depend almost entirely upon the assumed nature of the primary process. The oxygen molecule provides one practical instance in which such dissociation is possible; other examples will be dealt with later. The general problem of the conditions necessary for primary dissociation has been greatly advanced within recent years as a result of the work, both theoretical and practical, of Franck and others. Franck (*Trans. Faraday Soc.*, **21,** 536, 1926; *Z. physikal. Chem.*, **120,** 144, 1926) has suggested the following mechanical picture of the coupling of vibrational with electronic excitation in a homopolar diatomic molecule.

It is assumed that when light is absorbed by a homopolar molecule, the specific act of absorption is confined to the electron system, and the potential energy of the nuclei is affected only indirectly and in so far as the raising of the electron system to another quantum state alters the strength of the chemical binding of the molecule. This change in the strength of the chemical binding may be large or small, positive or negative. A schematic representation of the potential energy of the nuclei as a function of their distance apart allows us to review the possible cases more easily.

The curve U in each of the diagrams of Fig. 32 represents the potential energy U of the two nuclei as a function of their distance apart r for the normal electronic state of the molecule. The value r_0 of r at the minimum of the curve gives the equilibrium nuclear separation in the non-vibrating state. For a given vibrational energy content U there are two values of r, the difference of which obviously gives the amplitude of the nuclear vibration. For large values of r the $U : r$ curve becomes horizontal and the height of this horizontal level above the minimum level measures the heat of dissociation D of the normal molecule. Each of the curves U' has the same meaning for the molecule in some state (n') of electronic excitation.

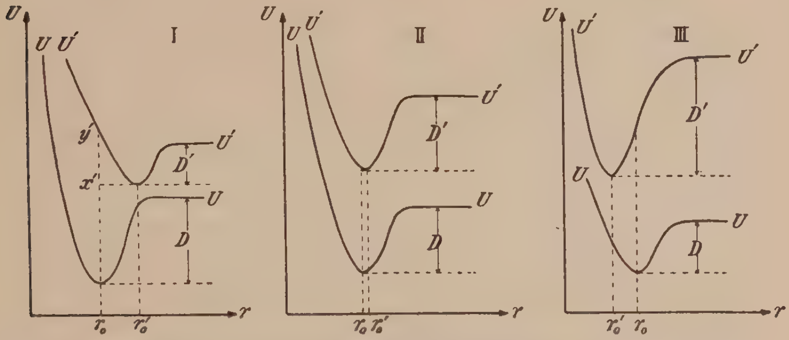

FIG. 32.—Potential energy of diatomic molecules plotted as a function of nuclear separation (after Franck).

Diagram I refers to the case where the chemical binding is very much weaker in the excited state of the molecule than in its normal state. Here we have $D > D'$. At the same time the equilibrium separation of the nuclei r_0' in the excited molecule is greater than the separation r_0 in the normal. We may represent absorption of radiation on the part of the normal non-vibrating molecule by passing from the minimum of the U curve vertically upwards to the U' curve. In the new condition of the molecule the potential energy $x'y'$ of the nuclei may be greater than D', the heat of dissociation of the molecule in state n', in which case the act of absorption results in dissociation. In a less extreme case where the potential energy $x'y'$ of the nuclei is not quite as great as D', the act of absorption does not involve dissociation but produces a very great change in the vibrational energy content, that is, in the vibration quantum number.

Diagram II shows the case where the chemical binding is practically independent of the state of electronic excitation of the molecule. For this case D' is practically equal to D and r_0' practically equal to r_0. Here the nuclei can gain little or no potential energy when the normal vibrationless molecule is excited by light, so that the change in the vibration quantum number will be small.

Diagram III shows a case where $r_0' < r_0$ and $D' > D$, that is, where the chemical binding is strengthened by the excitation process. Whether the vibration quantum number now increases or decreases as a result of excitation depends upon the particular form of the potential energy curves. If we assume that the case considered is the converse of that of Diagram I, we may expect that a molecule which is oscillating strongly in the initial (lower) state can use up all or the greater part of its vibrational energy in the excitation of the electron system.

It is not of course necessary to limit the use of this diagrammatic mode of visualisation to the process of excitation of the normal molecule; the reverse transition from excited to normal state, and transitions between different excited states, whether in emission or in absorption, may be pictured in the same way. In all cases, however, we must be careful not to interpret the result too literally. For example, with Diagram I it must be emphasised that the normal vibrationless molecule is not actually restricted to the sole act of absorption which would give (momentarily) an excited molecule with potential energy corresponding to point y'. All that the picture can be taken to mean is that this transition is the most probable, that is, the frequency corresponding to it will be most intensely absorbed. On this basis a theory of the distribution of intensity in band systems has been developed by Condon (*Phys. Rev.*, **28**, 1182, 1926). In order to forecast with any certainty the favoured transitions in the molecule, it is necessary to know the exact shapes of the pertinent $U : r$ curves. These can be drawn in some cases from a knowledge of various parameters of the molecule derived from the spectral data. Without entering into details, the general result is as above that for a large change in the strength of the chemical binding, as evidenced by a large change in the moment of inertia or by a large difference in the β's characterising the two combining electronic states of the molecule, the favoured transitions in emission and in absorption should be those involving a large change in the vibration quantum number p. On the other hand, with approximate independence of the chemical binding and therefore of I or β on the state of excitation, we should expect very small changes in p to be favoured. Several examples of band groups which conform to these intensity rules are treated in detail by Condon.

Reverting to a consideration of the possibility of primary dissociation of molecules by absorption of radiation, we can now see why it is that this should occur for oxygen, but not for nitrogen. In the case of oxygen the sub-levels of the electronic state B are very closely spaced compared with those of the normal state X—the β's are 708 and 1565 cm.$^{-1}$ respectively—so that there is evidently a very great loosening of the chemical bond when the molecule passes from X to B. This is further borne out by the two values of the nuclear separation $r_0 = 1{\cdot}21 \times 10^{-8}$ and $r_0' = 1{\cdot}61 \times 10^{-8}$ cm. for the normal and the excited states as calculated from the moments of inertia. We should expect then, from what we have said regarding Diagram I, that when the normal vibrationless molecule of oxygen ($p_X = 0$) is excited by absorption to the electronic state B, there should be a decided preference for large values of p_B in the observed bands. In agreement with this, the strongest absorption bands in oxygen run from $p_B = 9$ to a limit at $p_B = 21$ with continuous absorption beyond. This continuous absorption corresponds to such an increase in the potential energy of the nuclei that it exceeds D' and dissociation occurs. We may mention that in the Runge emission bands of oxygen, which involve the reverse type of transition $B \rightarrow X$, the same preference for large alterations in the vibration quantum number is found, the actual bands being $p_B = 0 \rightarrow p_X = 11$ to 17.

For nitrogen it is true that the electronic state A' which combines with the normal state X in absorption represents also a somewhat weaker chemical binding than the normal state—β equals 1679 as compared with 2345 cm.$^{-1}$. However, the weakening is not so pronounced as in the case of oxygen—in fact the nitrogen case lies midway between those represented by Diagrams I and II—so that we should not anticipate very large alterations in the vibration quantum number in the observed ultra-violet band group, and in particular we should not expect to find an experimental convergence limit to the system of absorption bands followed by a region of continuous absorption as in the case of oxygen. This is in agreement with experience. The photochemical dissociation of nitrogen by absorption of radiation does not appear to be feasible.

Photo-Dissociation of the Halogens.—The halogens were the first examples cited by Franck for which primary dissociation may occur in an elementary act of absorption. For various reasons these molecules deserve special consideration. The band absorption spectra of chlorine, bromine, and iodine vapours at ordinary temperatures have all been thoroughly investigated within recent years—iodine by Pringsheim (*Z. Physik*, **5**, 130, 1921) and by Mecke (*Ann. Physik*, **71**, 104, 1923), bromine and chlorine by Kuhn (*Z. Physik*, **39**, 77, 1927). All the vapours show a very complex band absorption in the long wave portion of the visible spectrum, the absorption stretching with increasing intensity from the red to the green and thereafter passing over into continuous absorption. In the latter respect the spectra clearly resemble that of oxygen, and absorption in the continuous region of the spectrum is therefore presumed to result in dissociation of the halogen molecule concerned. The relatively great complexity of the band absorption of the halogens as compared with that of oxygen admits of the following straightforward explanation. The chemical binding of the atoms in the normal oxygen molecule is very strong, and the first vibration quantum of the molecule is correspondingly high—actually about 4400 calories per mole. For this reason, at ordinary temperatures practically every oxygen molecule starts from the vibrationless state, and in the absorption spectrum there is but a single progression of bands—a Deslandres second progression—all deriving from one and the same initial state of the absorbing molecule. On the other hand, in the normal halogen molecule the chemical binding is relatively weak, the first vibration quantum being only about 600 calories for iodine, 900 calories for bromine, and 1600 calories for chlorine. For this reason it is to be anticipated that even at ordinary temperatures an appreciable fraction of halogen—and especially iodine—molecules exist in vibrational states above the first. The absorption spectrum of the non-vibrating normal molecule would consist of one single second progression of bands; that of the molecule thermally endowed with one quantum of vibrational energy previous to absorption would consist of another and different second progression, and so on. These various possible progressions give, by overlapping, the complex system of bands which is actually observed.

Iodine.—In the visible * absorption spectrum of iodine at temperatures from 70° to 200° C. there are over 130 bands stretching from about 700 to 500 $\mu\mu$; beyond this lies the region of continuous absorption which stretches up to 430 $\mu\mu$. Mecke (*loc. cit.*) has carried out an exhaustive analysis of the positions of the observed band edges, and arranged them into ten different progressions which partially overlap and each of which converges towards the blue. Interpreting these as second progressions, the separations of adjacent edges in any one progression give the successive vibration quanta of the excited molecule, and the separations of corresponding edges in consecutive progressions give the successive vibration quanta of the normal molecule. The progression in which we are specially interested is that to which the region of strong continuous absorption is attached. This is *the shortest wave-length progression*, beginning at about 570 $\mu\mu$ and extending right to the convergence limit which lies at 499·5 $\mu\mu$. Between 570 and 503 $\mu\mu$ it contains 42 separable bands, and there are a few further members between 503 and 499·5 $\mu\mu$ which are not separately resolved. The identification of the initial state of the molecule which absorbs the bands of this progression is made possible by Pringsheim's observation that with increasing temperature of the absorbing vapour this particular progression is somewhat weakened in intensity, whereas all the other progressions are strengthened, the neighbouring one slightly, the farther ones considerably. Now from the Boltzmann principle the number of non-vibrating molecules in a gas is always diminished by increase of temperature, but the number of molecules in any definite state of vibration is always increased, and proportionately the more the higher the state of vibration in question.

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* Iodine shows another region of band absorption in the ultra-violet which bears no relation to the spectrum at present under consideration.

From this it follows that it is the non-vibrating iodine molecule which absorbs the bands of the shortest wave-length progression. This conclusion, while at variance with Mecke's original ascription of vibration quantum numbers to the bands, is supported by the results of observations on the fluorescence of iodine vapour.

The strength of the chemical bond in the normal iodine molecule falls off very slowly with increasing vibrational energy content. This is shown by the fact that while the value of the first vibration quantum is 213 cm.$^{-1}$, that of the ninth vibration quantum has only fallen to 203 cm.$^{-1}$.* The chemical bond in the optically excited molecule is much weaker than in the normal—the first vibration quantum in the excited state is only 126 cm.$^{-1}$—and moreover the strength of binding falls off rapidly with increasing vibrational energy. It is due to both these circumstances that the normal molecule is able to absorb appreciably right up to the convergence limit and beyond, increasing its vibration quantum number by the act of absorption to such a degree that the resultant vibrational energy content exceeds the amount D' required to dissociate the excited molecule. The case of iodine provides a perfect illustration of the conditions depicted in Franck's Diagram I.

The position of the convergence limit which marks the transition from discontinuous to continuous absorption is accurately fixed at $\lambda_c = 4995$ Å by a short extrapolation from the last resolved band at 503 $\mu\mu$. Expressing the wave-length λ_c in energy units, it follows that the minimal energy required to effect the optical dissociation of the normal non-vibrating molecule is 2·469 volts or 56,950 calories per mole. This value, however, greatly exceeds the ordinary heat of dissociation of iodine, derived from chemical data, which is about 35,000 calories. Franck therefore infers that the products of the optical dissociation cannot be two normal atoms of iodine, but must be one normal atom and one internally excited atom. Fortunately it is possible to decide unequivocally from the series spectrum of the iodine atom what the actual amount of excess energy associated with this excited atom must be, and hence to obtain an accurate estimate of D from spectroscopic data alone. The fundamental term in the arc spectrum of each halogen atom is a doublet designated by $2^2P_{1,2}$. The larger component 2^2P_2 corresponds to the normal energy level of the atom, the other component 2^2P_1 to a metastable condition. Having regard for the total amount of energy supplied for the act of optical dissociation of the molecule, the possibility of states of excitation of the resultant halogen atoms higher than this metastable state need not be considered. The term differences $(2^2P_2 - 2^2P_1)$ for chlorine, bromine, and iodine were first computed roughly by Franck, and later measured directly from the arc emission spectra of the halogens by Turner (*Phys. Rev.*, **27,** 397, 1926). The term difference for iodine is 0·937 volt (cf. Table XXI., p. 222). This means that the metastable iodine atom possesses 0·937 volt or 21,600 calories of internal energy above the normal content. If we now assume that dissociation of the normal molecule by absorption at the convergence position 4995 Å results in a normal and a metastable atom, we have

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* Actually, from the fluorescence bands of iodine the first 37 vibrational sub-levels of the normal state of the molecule are now known. On account of the slow convergence, however, a very long extrapolation to zero spacing is indicated, so that the heat of dissociation D can only be very roughly estimated therefrom. The so calculated value of D is about 38,000 calories as compared with the thermal value of 35,000 calories.

$$h\nu_c = D + (2^2P_2 - 2^2P_1),$$

where $h\nu_c$ is the quantum absorbed and D is the ordinary heat of dissociation. Substituting $h\nu_c = 2{\cdot}469$ volts and $(2^2P_2 - 2^2P_1) = 0{\cdot}937$ volt, we obtain $D = 1{\cdot}532$ volts or 35,300 calories. This is in good agreement with the original chemical estimate of Bodenstein and Starck (*Z. Elektrochem.*, **16,** 966, 1910) of 34,500 calories and with Braune and Ramstetter's more recent estimate (*Z. physikal. Chem.*, **102,** 480, 1922) of 35,100 calories. The numerical agreement must be considered to vindicate completely Franck's assumption regarding the nature of the products of the optical dissociation. We may remark that the value $D = 35{,}300$ calories which is computed from spectroscopic data alone is likely to be the most accurate, since the measurements of ν_c and $(2^2P_2 - 2^2P_1)$ upon which it depends can be made with optical precision.

Finally we may briefly mention an experiment of Dymond (*Z. Physik*, **34,** 553, 1925) which Franck quotes in support of the thesis that dissociation of iodine does actually take place when the molecule absorbs in the continuous region. By illumination of iodine vapour with a series of wave-lengths on the long wave side of the convergence limit at 4995 Å, the vapour is excited to emit molecular band fluorescence. Illumination with wave-lengths shorter than 4995 Å, however, produces no trace of fluorescence in the vapour, although such wave-lengths are more strongly absorbed than those in the region of band absorption. This result is easily explicable if we assume that absorption in the continuous region dissociates the molecule; there would then be no possibility of re-emission of the absorbed energy.

Bromine.—The band absorption spectrum of this vapour in the visible at ordinary temperatures has recently been measured and analysed by Kuhn (*loc. cit.*). The first band lies at 672 $\mu\mu$, and between this and the point at about 510 $\mu\mu$ where true continuous absorption begins (but excluding a narrow region between 528 and 555 $\mu\mu$ wherein only an unordered medley of lines, but no obvious band edges, are to be detected) nearly seventy band edges have been observed. These are arranged by Kuhn into six progressions. The different progressions all converge towards the blue, and accordingly they characterise different initial states of vibration of the absorbing bromine molecules. For the purpose of illustrating the nature of these progressions, the wave-numbers (ν) of the members of all six, with the vibration quantum numbers in the initial (p') and final (p'') states as ascribed by Kuhn, are given in Table XX. In the table, the *vertical differences* ($\Delta''\nu$) between the wave-numbers of consecutive bands in any one progression give the magnitudes of successive vibration quanta in the excited molecule. The criteria which govern

TABLE XX.

ABSORPTION BAND SYSTEM OF BROMINE.

p'' ↓	$p' = 5$.		$p' = 4$.		$p' = 3$.		$p' = 2$.		$p' = 1$.		$p' = 0$.	
	ν	$\Delta''\nu$	ν	$\Delta''\nu$	ν	$\Delta''\nu$	ν	$\Delta''\nu$	ν	$\Delta''\nu$	ν	$\Delta''\nu$
0	14877	152	15184	150								
1	15029	139	15334	146	15650	146						
2	15168	146	15480	144	15796	140						
3	15314	137	15624	139	15936	140						
4	15451	136	15763	133	16076	136						
5	15587	129	15896	131	16212	131	16528	133				
6	15716	123	16027	127	16343	128	16661	126	16981	125		
7	15839	125	16154	125	16471	124	16787	123	17106	125		
8	15964		16279	120	16595	119	16910	122	17231	127		
9			16399	116	16714	117	17032	121	17358	116		
10			16515		16831	113	17153		17474	99	17799	100
11					16944				17573	98	17899	
12									17671	94		
13									17765	87		
14									17852			
15												
16												
17												
18												
19											18998	55
20											19053	51
21											19104	42
22											19146	47
23											19193	41
24											19234	40
25											19274	34
26											19308	38
27											19346	23
28											19369	33
29											19402	23
30											19426	24
31											19450	19
32											19469	19
33											19488	14
34											19502	13
35											19515	14
36											19529	11
37											19540	

the assignment of the p'''s are (1) $\Delta''\nu$ should fall off regularly in each column, and (2) all the $\Delta''\nu$'s lying in a horizontal row should be equal. An examination of the table shows that both these criteria are satisfied within the limits of accuracy of the ν's. Similar rules govern the assignment of the p''s, viz. (1) the *transverse differences* $\Delta'\nu$ (not tabulated) between corresponding bands in adjacent progressions should fall off regularly from right to left of the table, and (2) all the transverse differences in a vertical column should be equal. The successive transverse differences $\Delta'\nu$ from right to left represent the magnitudes of the successive vibration quanta in the normal molecule. The averaged values of these are as follows :—

	$p' = 4 \rightarrow 5$	$p' = 3 \rightarrow 4$	$p' = 2 \rightarrow 3$	$p' = 1 \rightarrow 2$	$p' = 0 \rightarrow 1$
$\Delta'\nu$(cm.$^{-1}$)	311	315	318	321	325

From these we see that, as in the case of iodine, the vibrational sub-levels of the normal bromine molecule converge very slowly, and since only the first five are known it would be impracticable to estimate the heat of dissociation of the normal molecule by extrapolating to $\Delta'\nu = 0$.

The largest vertical difference in the table $\Delta''\nu = 152$ cm.$^{-1}$ represents the first vibration quantum of the excited molecule. Since this is less than half the first vibration quantum of the normal molecule, the chemical binding of bromine is considerably weaker in the excited than in the normal state. The conditions are thus favourable for the large changes in the vibration quantum number which are requisite for primary dissociation of the molecule by absorption. In agreement with this, we see that the first band ($\nu = 17799$ cm.$^{-1}$) of measurable intensity absorbed by the normal non-vibrating molecule already corresponds to a change in vibration quantum number of ten units. From this point, the intensity of absorption in the $p' = 0$ progression gradually increases and reaches a maximum within the region of continuous absorption which is appended to the convergence limit of the progression. This shows that the elementary act of absorption by the vibrationless molecule of greatest *a priori* probability involves such a large alteration in p that dissociation results. That the bands in the progression labelled $p' = 0$ actually do correspond to the vibrationless state as initial state in absorption has been proven by Kuhn from the temperature-intensity relations of the progressions. When the absorbing vapour is raised from 20° C. to 550° C. the intensity of absorption of the progression $p' = 0$ and of the continuous region attached thereto is somewhat diminished, whereas all the other progressions increase in intensity.

As will be seen from the table, the value of $\Delta''\nu$ falls off rapidly with increasing p'', and for the two last separable band edges of the $p' = 0$ progression ($p'' = 36$ and 37) the separation is only 11 cm.$^{-1}$ or 3 Å. By a very short extrapolation the exact position of the convergence limit (a position which is masked on the spectrogram by the fact that beyond the band $p'' = 37$ it is practically impossible to distinguish apparent from true continuity) is fixed at $\nu_c = 19{,}580$ cm.$^{-1}$ or $\lambda_c = 5107$ Å. This estimate of λ_c is considered to be correct to within a few Ångstrom units. Assuming as in the case of iodine that absorption at the convergence limit just suffices to dissociate the normal non-vibrating bromine molecule into a normal and a metastable atom, we have again

$$h\nu_c = D + (2^2P_2 - 2^2P_1).$$

The value of $h\nu_c$ is 2·415 volts, and Turner's value (cf. Table XXI.) of the term difference $(2^2P_2 - 2^2P_1)$ for the bromine atom is 0·454 volt, whence D is 1·961 volts or 45,200 calories per mole. This spectroscopic value for D is in good accord with Bodenstein's value (*Z. Elektrochem.*, **22**, 338, 1915) of 46,200 calories, derived from the dependence of the thermal equilibrium $Br_2 \rightleftharpoons 2Br$ upon the temperature.

Chlorine.—Appreciable band absorption begins with chlorine gas at ordinary temperatures at about 580 $\mu\mu$. Between this point and the beginning of the region of true continuous absorption at about 478 $\mu\mu$, Kuhn has located about fifty band edges. The intensity of absorption in this band system increases more or less regularly as we pass towards the convergence limit of the bands, but the absorption maximum lies well beyond the convergence limit in the region of continuous absorption at 334 $\mu\mu$. The chlorine bands have been arranged by Kuhn into five progressions, each converging towards the blue. As in the preceding cases, it is the shortest wave-length progression which carries the convergence limit and the subsequent region of continuous absorption. However, this shortest wave-length progression of bands cannot in the present case be taken to derive from absorption by the normal non-vibrating molecule. If this were so, these bands should diminish in intensity and the bands of the other four progressions increase in intensity when the temperature of the absorbing gas is raised. Instead of this, however, it is found that the intensities of *all* the bands in all five progressions are markedly increased by elevation of the temperature. By measuring this temperature effect and utilising the Boltzmann principle, Kuhn has shown that the bands of the shortest wave-length progression must derive from chlorine molecules which already possess one quantum of vibrational energy before absorbing. Accordingly, the five progressions correspond in order of increasing wave-length to $p' = 1, 2, 3, 4$, and 5. The reason why no bands corresponding to a $p' = 0$ progression are observed for chlorine will be discussed shortly.

From the averaged differences between the ν's of corresponding bands in the different progressions, the second, third, fourth, and fifth vibration quanta of the normal molecule work out to be 557, 546, 541, and 525 cm.$^{-1}$ respectively. By extrapolation, the first vibration quantum of the normal molecule should be about 565 cm.$^{-1}$ or 0·070 volt. The bands of the shortest wave-length progression ($p' = 1$) converge rapidly, and only a very short extrapolation of the series beyond the last resolved member is required to fix the position of their convergence limit and the beginning of the region of true continuous absorption at $\nu_c = 20{,}900$ cm.$^{-1}$ or $\lambda_c = 4785 \pm 7$ Å. Remembering that the chlorine molecule which is dissociated by absorption of λ_c possesses one vibration quantum $h\nu_1$ previous to the act of absorption, the heat of dissociation D of the normal *non-vibrating* molecule into normal atoms is now given by

$$h\nu_c = D + (2^2P_2 - 2^2P_1) - h\nu_1.$$

Here $h\nu_c$ is 2·577 volts, $h\nu_1$ is 0·070 volt, and the term difference $(2^2P_2 - 2^2P_1)$, which is the excess energy content of the metastable chlorine atom resulting from the optical dissociation, is 0·109 volt. The spectroscopic value for D is therefore 2·538 volts or 58,500 calories, a value which may be compared with the most recent chemical estimate of 57,000 calories obtained by Wohl and Kadow (*Z. physikal. Chem.*, **118**, 460, 1925).

For convenience of reference, the important spectral data for the three halogens are collected together in the following table :—

TABLE XXI.

	λ_c(Å).	$h\nu_c$ (Volts).	$2^2P_2 - 2^2P_1$ (Turner).		D (Spectroscopic).		D (Thermal) Calories.
			Volts.	Calories.	Volts.	Calories.	
Iodine	4995	2·469	0·937	21,600	1·532	35,300	35,100
Bromine	5107	2·415	0·454	10,500	1·961	45,200	46,200
Chlorine	4785	2·577	0·109	2,500	2·538	58,500	57,000

We must now enquire (*a*) why no bands of a $p' = 0$ progression are observed in the absorption spectrum of chlorine, and (*b*) in the absence of such bands what part of the observed spectrum does correspond to absorption by the non-vibrating molecule. The bulk of the absorption of the gas at ordinary temperatures should, of course, be due to these molecules, since from the magnitude of the first vibration quantum (565 cm.$^{-1}$ or 1600 calories) it can be calculated that for thermal equilibrium about thirteen-fourteenths of the chlorine molecules are in the vibrationless state.* The spectral position which the $p' = 0$ progression should occupy can easily be computed from the fact that each band of the progression should be displaced by the same amount towards the violet from the corresponding band of the progression $p' = 1$, the amount of the displacement being $\Delta'\nu = 565$ cm.$^{-1}$. In particular, the convergence limit of the $p' = 0$ progression should lie 565 cm.$^{-1}$ to the left of that of the $p' = 1$ progression, that is, at $\nu = 20{,}900 + 565 = 21{,}465$ cm.$^{-1}$ or $\lambda = 4659$ Å. The relative positions of the two progressions are shown in Fig. 33.

From the figure we see that the continuous absorption to the right of $\lambda = 4659$ Å is due solely to vibrating ($p' = 1$) molecules ; to the left of 4659 Å the continuous absorption is due to both vibrating ($p' = 1$) and non-vibrating ($p' = 0$) molecules. Passing from $\lambda =$ 4659 Å towards the ultra-violet, the non-vibrating molecule becomes

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[*] This fraction is given approximately by the expression $1 - e^{-1600/RT}$.

the main contributor, and probably the absorption at the maximum ($\lambda = 334\ \mu\mu$) is due solely to this molecule. The probable distribution of intensity in the $p' = 0$ progression may be inferred as follows. From Kuhn's data, the first vibration quantum of the excited molecule is about 180 cm.$^{-1}$. Comparing this with the first vibration quantum of the normal molecule, we see that the chemical binding of chlorine in the excited state is very much weaker than in the normal state. The case is even more extreme than that of bromine or of iodine, and we may expect that the favoured acts of absorption on the part of the vibrationless molecule will involve specially large changes in p. It is not surprising then that the *bands* of the $p' = 0$ progression which would lie to the right of $\lambda = 4785$ Å are not detectable, or that the bands which possibly lie between 4785 and 4659 Å are completely obscured by the continuous absorption region of the $p' = 1$ progression. For bromine, the maximum of absorption of the $p' = 0$ progression lies about 900 Å to the left of the convergence point. For chlorine, the corresponding maximum coincides in all probability with the observed maximum of continuous absorption at 334 $\mu\mu$ and lies 1320 Å to the left of the convergence point of the $p' = 0$ progression.

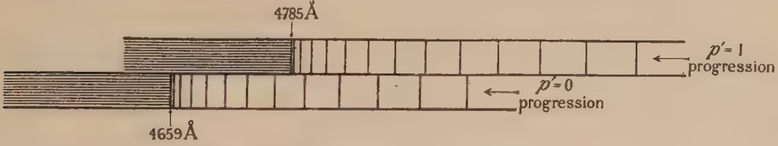

FIG. 33.—Schematic representation of the $p' = 0$ and $p' = 1$ progressions of absorption bands of chlorine.

Sulphur, Selenium, and Tellurium.—These substances, which are the chemical homologues of oxygen, provide further examples of the occurrence, under properly chosen conditions, of the optical dissociation of homopolar molecules into atoms. The absorption and fluorescence spectra of all three vapours in the spectral region between 700 and 200 $\mu\mu$ have recently been examined in detail by Rosen (*Z. Physik*, **43,** 69, 1927). In each case the absorption spectrum, which is associated under the conditions of observation with the diatomic molecule, consists of a complex system of diffuse bands, each degraded towards the red. The regions of discontinuous band absorption are

S_2 : 4000 — 2548 Å ; Se_2 : 4180 — 3238 Å ; Te_2 : 6200 — 3831 Å.

As with the halogens, the discontinuous spectrum is followed in each case by a region of strictly continuous absorption. Making use of the criteria already indicated in other cases and with the help of information drawn from the fluorescence spectra, Rosen has succeeded in resolving each complex group of bands into a number of second progressions, each progression converging towards the violet and each corresponding to absorption by molecules which possess a definite initial amount of vibrational energy ($p' = 0, 1, 2, 3$, etc. progressions). He has also obtained the correct assignment of the vibration quantum numbers p' and p'' of the initial (normal) and final (excited) states concerned for each band. From this it appears that the region of continuous absorption attaches in each case to the $p' = 0$ progression, that is, it is the normal non-vibrating molecule which is dissociated by absorption in the continuous region. The existence of this region corresponding to optical dissociation of the molecule in the present instances agrees with the circumstance—laid down by Franck as the primary condition for such dissociation—that the strength of the nuclear binding in the normal state of the molecule is much greater than that in the excited state. These strengths of binding are represented approximately by the β' (normal) and β'' (excited) coefficients of the band group equation (27), which according to Rosen's measurements have the following values :—

Element.	β'(cm.$^{-1}$).	β''(cm.$^{-1}$).
Te_2	250·4	163
Se_2	397·5	247·2
S_2	724·5	424·4
O_2	1565·4	708

For purposes of comparison the values of the β's for the homologous element oxygen are also included.

From the optical data Rosen has attempted to estimate the heats of dissociation of the S_2, Se_2, and Te_2 molecules into normal atoms by the two methods already described in the preceding pages. We need only give the results for sulphur. By the first method—extrapolation of the vibrational sub-levels of the normal state of the molecule to zero separation—a value of D of 128,000 calories is obtained. This estimate is admittedly very rough, since the normal sub-levels only converge very slowly and the necessary extrapolation is long and uncertain. By the second method, D is to be derived from the long wave limit of the region of continuous absorption (the convergence position of the $p' = 0$ progression of bands) where absorption just suffices to dissociate the molecule. Unfortunately in the case of sulphur the exact position of this long wave limit is not known very accurately; it lies at $\nu_c = 40{,}000 \pm 1000$ cm.$^{-1}$ Furthermore, it is uncertain—as with oxygen (cf. p. 208)—what particular electronic energy levels the atoms which result from the optical dissociation should occupy; the fundamental spectral term of the sulphur atom is a triplet, the members of which correspond to the normal and two metastable states at the energy levels 0·02 and 0·07 volt respectively. The extreme possibilities as regards the resultants of the optical dissociation are (*a*) two normal atoms, and (*b*) two metastable atoms with a total excess energy content of 0·14 volt or 1130 cm.$^{-1}$. Having regard for these uncertainties, the value of D works out to 112,000 ± 5000 calories. This estimate, which should be accurate within the limits indicated, is definitely higher than the very rough value for D of 90,000 calories obtained by Wartenberg (*Z. anorg. Chem.*, **56,** 332, 1908) by chemical methods. The absorption spectrum of sulphur vapour is further considered later in this Chapter.

THE OPTICAL DISSOCIATION OF HETEROPOLAR MOLECULES.

We have seen from the foregoing Section that the dissociation of a homopolar diatomic molecule is sometimes possible in an elementary act of absorption, the products of dissociation being neutral atoms one of which is in the normal, the other in an activated state. This optical dissociation is in some ways analogous to the photo-ionisation of an atom which occurs when it absorbs a frequency beyond the convergence limit of its Principal Series. The latter process, however, would be more properly paralleled by the optical splitting of a *heteropolar* molecule into a positive and a negative ion. One conceivable way of splitting a molecule built up of two ions into its constituents is by increasing the vibrational energy of the normal molecule to the necessary extent by absorption at or beyond the convergence limit of its infra-red vibration bands. Actually, however, such a convergence limit is never realised in practice, only the first few overtones of the fundamental infra-red vibration band being ever absorbed with measurable intensity. Another conceivable means of splitting the ionic molecule into ions would be by absorption in such a spectral region as to cause the displacement of an electron in the atmosphere of one or other of the constituent ions. If this displacement involved a considerable modification in the binding force of the ions, it might be that the increase in the vibration quantum number coupled with the electronic transition would be sufficient to cause dissociation of the molecule—not into two normal ions, however, but into a normal and an excited ion. We do not know whether such an optical process has ever been realised; certainly the necessary frequency would in most cases lie in the extreme ultra-violet, since the electron atmospheres of the ions are of the inert-gas type, and corresponding to this any electron in the ionic molecule should be extremely difficult to displace in the manner indicated.

Apart from the above possibilities, recent observations by Terenin, Franck, and others have shown that the optical dissociation of heteropolar molecules often does occur, the molecule being split by the act of absorption, not into ions as above conceived, but into two neutral components (atoms in the case of dipole molecules). In dealing with the various cases which have been studied in this connection, it is found necessary to distinguish between two types of heteropolar linkages. The one type, as exemplified by most of the simple metal salts such as the alkali halides, are characterised by ionic lattices in the crystal state and by marked electrical conductivity in the liquid and dissolved states. Such molecules as these are considered to be true ionic structures, the molecule resulting from the union of the neutral atoms by the complete transfer of one or more of the peripheral electrons of the metal radical to the acid radical. On the other hand, there are a great number of compounds the molecules of which are also polar but which cannot be regarded as ionic linkages in the above sense. These substances form atomic or molecular lattices in the crystal state and they normally have a poor electrical conductivity in the solid, liquid, and dissolved states. These are essentially atom compounds, and the polarity of their molecules is therefore to be ascribed to some asymmetry in the grouping of the peripheral electrons in the molecule which gives it an intrinsic electric moment; the peripheral electrons are not, however, segregated as in the ionic molecule. To the category of heteropolar atom compounds belong such substances as CO_2, H_2O, NH_3, HCN, the hydrogen halides, and probably most organic compounds. It may be noted that the possession of an infrared vibration band spectrum does not necessarily imply an ionic structure for the molecule concerned, but only an intrinsic electric moment.

Confining ourselves to the consideration of polar diatomic molecules, we must suppose that if by some means the vibrational energy content of an ionic dipole were progressively increased without the electronic systems of the molecule being simultaneously excited, dissociation into ions would occur. If, however, the vibrational energy content of a non-ionic dipole were similarly increased, the products of dissociation would be the neutral atoms. In this particular, there appear to be no grounds for differentiating between the dipolar atom linkage and the homopolar linkage. From the experimental standpoint, it further appears that the optical dissociation of a dipolar non-ionic molecule and that of a homopolar molecule are also exactly analogous as regards the nature and condition of the dissociation products. In both cases neutral atoms are formed, one of them in the normal, the other in an excited state. The fact that the optical dissociation of such molecules does not (at least in any case so far investigated) result in *two* normal atoms may be explained by the following (admittedly imperfect) argument. The act of absorption of radiation by the molecule is primarily coupled, not with a loosening of the chemical bond, but with the displacement of one of the peripheral electrons from its normal orbit. Dissociation of the molecule into atoms follows if the potential energy function of the chemical binding happens to be suitably modified as a result of the electron's displacement. This electron is, however, a peripheral electron in one of the resultant atoms, and unless it occupies in the normal molecule a lower quantum orbit than in the normal atom, we should naturally expect its displacement to be reflected in the condition of this atom after the molecule splits into its components.

In contrast to the homopolar and dipolar non-ionic molecules, the true ionic molecule is found to admit of optical dissociation not only into neutral atoms one or both of which are excited, but also into neutral atoms which are *both* in the normal state. In order that the ionic molecule should dissociate into neutral atoms of any kind we must suppose that (*a*) the electronic transition coupled with the act of absorption corresponds to the transfer of an electron from the anion part to the cation part of the molecule, and (*b*) the non-ionic structure thus formed represents a much looser chemical binding than does the original molecule. Granted these, the energy conditions of the resultant atoms depend upon the exact nature of the electronic transition mentioned in (*a*). If this is such that the transferred electron takes up its most stable orbit in the cation and leaves the anion in its most stable configuration, then, of course, dissociation into neutral and normal atoms results. This, however, is only the first of four different possibilities of dissociation into neutral atoms, which may be represented as follows :—

$$\left\{\underset{e}{\overset{M^{+}\;X^{-}}{\curvearrowleft}}\right\} \rightarrow \{M\ .\ .\ X\} \rightarrow M + X \quad . \quad . \quad . \quad (1)$$

$$\left\{\underset{e}{\overset{M^{+}\;X^{-}}{\curvearrowleft}}\right\} \rightarrow \{M^{*}\ .\ .\ X\} \rightarrow M^{*} + X \quad . \quad . \quad . \quad (2)$$

$$\left\{\underset{e}{\overset{M^{+}\;X^{-}}{\curvearrowleft}}\right\} \rightarrow \{M\ .\ .\ X^{*}\} \rightarrow M + X^{*} \quad . \quad . \quad . \quad (3)$$

$$\left\{\underset{e}{\overset{M^{+}\;X^{-}}{\curvearrowleft}}\right\} \rightarrow \{M^{*}\ .\ .\ X^{*}\} \rightarrow M^{*} + X^{*} \quad . \quad . \quad . \quad (4)$$

From (1) two normal atoms result, from (2) or from (3) one normal and one excited atom, from (4) two excited atoms. The first three at least of these four possibilities have been realised experimentally.

Alkali Metal Halides.—We must now give a brief survey of the experimental observations on the basis of which the optical dissociation of heteropolar molecules and the above differentiation between ionic and non-ionic linkages have been established. As examples of diatomic molecules which are definitely ionic in character we may take the alkali metal halides. The first experimental evidence for the optical dissociation of such molecules derives from Terenin's observation (*Z. Physik*, **37,** 98, 1926) that when the vapour of sodium iodide is illuminated with ultra-violet light of wave-length below 2450 Å, a strong yellow fluorescent emission of the D lines, characteristic of the free metal atom, is obtained. Beyond this, there is no indication of any other lines or bands in the fluorescence unless the wave-length of the exciting light falls to 1854 Å when the second doublet 3302/3 Å of the Principal Series of sodium flashes out, the intensity of emission simultaneously decreasing markedly. The fact that other sodium lines do not appear in the luminescence shows that ionisation of free sodium atoms (formed by thermal dissociation of the salt vapour) is not a preliminary to the fluorescent emission—otherwise the whole arc spectrum of sodium should be observed. It was further inferred and later proven conclusively by Terenin that the luminescence cannot be due to a secondary excitation of free sodium atoms by collision with optically excited NaI molecules. Two possibilities then remain—either the excited sodium atom which emits the D or the 3302/3 Å doublet results from disruption of an optically excited NaI molecule by collision with another NaI molecule thus :—$NaI^* + NaI \rightarrow Na^* + I + NaI$, or it is formed directly by the optical dissociation of the salt molecule in an elementary act of absorption, viz. :—$NaI + h\nu \rightarrow Na^* + I$. The first of these alternatives was that originally suggested by Terenin (*loc. cit.*), but later observations by Kondratjew (*Z. Physik*, **39,** 191, 1926) and by Terenin himself (*ibid.*, **44,** 713, 1927) on the dependence of the luminescence upon the wave-length of the exciting radiation, the pressure of the salt vapour itself, and that of added " inert " gases, proved that the phenomena must be ascribed to the primary dissociation of the salt molecule into an excited metal atom and a normal halogen atom. The same emission of atom lines associated with the optical dissociation of other salt molecules has been observed—for CsI by Kondratjew, and for TlBr, TlI, and CuI by Terenin. The view that the excited metal atom results directly from the dissociation of the salt molecule is strikingly confirmed by the energy relations shown in Table XXII. Here E is the minimum amount of radiant energy (calculated from the long wave-length limit of the exciting spectral region) required to excite the salt vapour to emit the atom line indicated in column (5), E_1 is the heat of dissociation of the salt molecule into normal atoms, and E_2 is the excess internal energy of the emitting metal atom. If the energy supplied by the radiation is just sufficient to dissociate the molecule into excited metal atom and normal halogen atom, then E should equal the sum of E_1 and E_2. This energy balance holds, within the limits of accuracy of the various data, for CsI and the two cases of NaI. In the case of TlI the energy supply apparently exceeds the required amount by about 0·3 volt (7000 calories). If this difference is real, it should appear as kinetic energy of relative translatory motion of the separating Tl* and I atoms, and should be evidenced by an anomalous

TABLE XXII.

Salt.	Limiting λ of Exciting Radiation (Approx.).	E (Volts).	Heat of Dissociation E_1.	Atom Line Emitted.	E_2.	$E_1 + E_2$.
NaI .	2450 Å	5·04	2·98	5896 Å	2·09	5·07
NaI .	1854 Å	6·70	2·98	3303 Å	3·74	6·72
CsI .	2080 Å	5·93	3·36	4593 Å	2·71	6·07
TlI .	2080 Å	5·93	2·35	3776 Å	3·27	5·62

broadening of the Tl emission line. While this has not been tested it has, however, been demonstrated by Franck and Hogness (*Z. Physik*, **44,** 26, 1927) that when the energy quantum actually absorbed by the NaI molecule is greatly in excess of what is required for its optical dissociation (by illuminating the NaI vapour with light of wave-length 2026 Å instead of the limiting wave-length for dissociation into Na* + I, viz. $\lambda = 2450$ Å), the Doppler broadening of the emitted D lines is about 0·1 Å, which is much greater than the normal broadening (0·03 Å) corresponding to the temperature of the system. It is clear from this that the resultant excited sodium atom is moving with a velocity greatly in excess of what it could attain thermally.

The absorption spectra of the alkali halide vapours in the ultra-violet have been investigated recently by Angerer and Müller (*Physikal. Z.*, **26,** 643, 1925), Müller (*Ann. Physik*, **82,** 39, 1927), and Franck, Kuhn, and Rollefson (*Z. Physik*, **43,** 155, 1927). The spectra obtained are strictly continuous and exhibit one or more selective absorption maxima. The long wave limit of the absorption region is slightly displaced towards longer wave-lengths with increasing temperature and pressure of the vapour, but the positions of the absorption maxima are practically independent of these variables. For each of the chlorides only one maximum is observed in the spectral region examined (viz. down to 230 $\mu\mu$). This maximum lies at about 246 $\mu\mu$ but its exact position depends to a slight extent on the nature of the cation, the limits being $\lambda_m = 2428$ Å for NaCl and $\lambda_m = 2485$ Å for RbCl. For each of the bromides there are two absorption maxima at about 276 $\mu\mu$ and 254 $\mu\mu$ respectively (the exact positions again depending on the nature of the salt), and there is a suggestion of the existence of a third maximum at still shorter wave-lengths. For the iodides there are also two observed absorption maxima at about 324 $\mu\mu$ and 258 $\mu\mu$ and definite indications of a third at some wave-length below 230 $\mu\mu$. The absorption curves for the sodium halides, which are more or less typical of their classes, are shown in Fig. 34.

These absorption data have been discussed and interpreted by Franck, Kuhn, and Rollefson (*loc. cit.*) in the following manner. The different continuous regions of absorption for the same molecule are supposed to be associated with its optical dissociation into different products. Thus for sodium iodide, absorption within the continuous band with maximum at 324 $\mu\mu$ effects the lowest stage of optical dissociation $\mathrm{NaI} + h\nu_1 \rightarrow \mathrm{Na} + \mathrm{I}$, the products separating with variable translatory velocities corresponding to the variability of ν_1, but without internal energy of excitation. Absorption within the continuous band with maximum at 258 $\mu\mu$ is responsible for the second stage of optical dissociation of the salt molecule, viz. $\mathrm{NaI} + h\nu_2 \rightarrow \mathrm{Na} + \mathrm{I}^*$, the resultant iodine atom being in the excited metastable 2^2P_1 state; while absorption in the presumed third band with maximum beyond 230 $\mu\mu$ causes one or other of the processes $\mathrm{NaI} + h\nu_3 \rightarrow \mathrm{Na}^* + \mathrm{I}$ or $\mathrm{NaI} + h\nu_3 \rightarrow \mathrm{Na}^* + \mathrm{I}^*$. It should be remarked that this allocation of the rôles of the different selective regions is not inconsistent with

Terenin's observation that illumination of sodium iodide vapour with light of wave-length 2450 Å causes the emission of the D lines. An excited sodium atom as dissociation product is on the above hypothesis associated with the continuous band with maximum below 230 $\mu\mu$, not with the preceding band with maximum at 258 $\mu\mu$ within which the wave-length 2450 Å falls. It is more than probable, however, that the two regions of continuous absorption overlap to a considerable extent, so that the wave-length interval between 240 $\mu\mu$ and 250 $\mu\mu$ is more or less common to the two.

The different dissociation processes applying in the different spectral regions can be tested in two ways. In the first place, the quantum absorbed at the long wave limit of continuous absorption (the convergence position of discontinuous band absorption) should be equivalent energetically to the thermal heat of dissociation of the salt molecule into normal atoms. Actually no such band convergence limit is shown in the spectrograms, the absorption being strictly continuous as far (towards longer wave-lengths) as any appreciable absorption is observed. This absence of a discontinuous region of absorption preceding the continuous region means, of course, that the probability of absorption by the molecule is only appreciable for such frequencies as are more than sufficient to effect the optical dissociation. This might indeed be inferred independently from the fact that the ionic linkage (normal state) is much stronger than the atom linkage (excited state) of the molecule, so that the probability that the potential energy of binding of the molecule when excited by absorption should exceed the energy of dissociation of the excited molecule is very great (cf. Diagram I of Fig. 32). In the absence of an observed convergence limit, we are forced to use the observed long wave limit of continuous absorption—the quantum absorbed there should be *ap-*

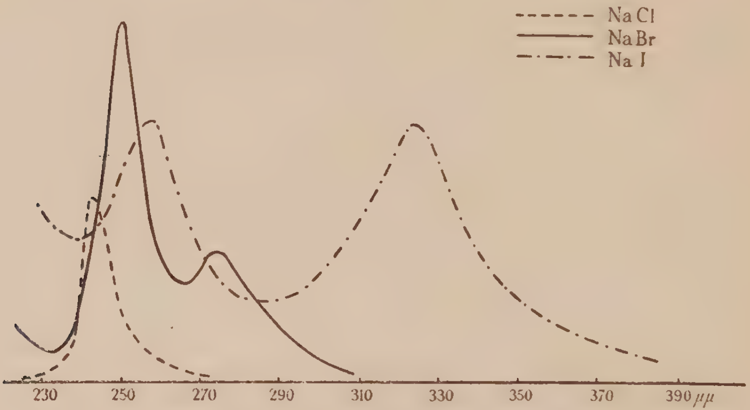

FIG. 34.—Ultra-violet absorption spectra of sodium halide vapours.

proximately equal to the heat of dissociation of the molecule into normal atoms. This prediction is more or less confirmed by a comparison of the figures in columns (3) and (4) of the succeeding table, representing respectively the optically calculated and thermally calculated values of D for different salts. Having regard for the approximate nature of the values calculated by either method, the agreement is all that can be expected.

TABLE XXIII.

Salt.	Long Wave Limit of First Absorption Region (Å).	D (Optical) Calories/Mole.	D (Thermal) Calories/Mole.
NaI . . .	>3900	<73,000	63,000
KI . . .	3800	75,000	84,000
CsI . . .	3800	75,000	75,000
NaBr . . .	3100	91,000	84,000
KBr . . .	3100	91,000	100,000
KCl . . .	2800	103,000	103,000

The conclusion that the first continuum corresponds to dissociation of the molecule into normal atoms is more completely vindicated by a consideration of the distances separating the successive absorption maxima of the bromides and iodides. Ascribing the long wave absorption region to decomposition into two normal atoms, the second absorption region should correspond to decomposition into a normal atom and an excited atom—in the present case, into a normal metal atom and a metastable ($2P_1$) halogen atom, since the excess energy of the metastable halogen atom is decidedly smaller than the amount of energy required for the first quantum jump of the alkali atom. Accordingly, the wave-numbers of the convergence positions of the first and second regions of continuous absorption should differ by an amount exactly equivalent to the term difference ($2P_2 - 2P_1$) between the normal and metastable levels of the halogen atom concerned. As already noted, however, these convergence positions are not known, so that perforce we must use in their stead either the observed limits of the pertinent absorption regions or, more conveniently in the present instance, the positions of the absorption maxima. By so doing, we cannot, of course, expect to obtain an *exact* equivalence between each difference $\nu_2(\text{max.}) - \nu_1(\text{max.})$ and the corresponding halogen term difference ($2P_2 - 2P_1$). The approximate agreement shown by the data of Table XXIV. is, however, sufficient evidence of the correctness of the general premises on which the comparison is based. It might be noted that for the chlorine atom the term difference ($2P_2 - 2P_1$) is only 880 cm.$^{-1}$ From this it is easy to see why for each chloride apparently only one absorption maximum is obtained. It is probable that, as for the bromides and iodides, both the photo-processes $MCl \rightarrow M + Cl$ and $MCl \rightarrow M + Cl^*$ take place, but the corresponding regions of absorption lie too close together for the separate existence of two absorption maxima to be verified.

TABLE XXIV.

Salt.	ν_2(max.) − ν_1(max.) cm.$^{-1}$	($2P_2 - 2P_1$) cm.$^{-1}$ (Turner).
NaI . . .	8000	7600
NaBr. . .	3300	3700
KBr . . .	3000	
RbBr. . .	3100	
Chlorides . .	—	880

There can be little doubt that an extension of the absorption measurements dealt with above beyond 230 $\mu\mu$ into the extreme ultra-violet will reveal further regions of selective absorption, corresponding to the decomposition of the absorbing halide molecules into alkali metal atoms excited to levels higher than the normal and halogen atoms in one or other of the doublet states ($2P_{1,\,2}$) of their fundamental level. For the bromides and iodides, at least, there is experimental evidence that a third region of selective absorption lies beyond the two discussed. In the case of sodium iodide, this third region which starts about 240 $\mu\mu$ may legitimately be associated with the photo-decomposition: NaI + $h\nu \rightarrow$ Na($2P$) + I, which Terenin finds, by the criterion of D line emission, to occur for wave-lengths below 245 $\mu\mu$. The quantum absorbed at 245 $\mu\mu$ corresponds almost exactly (cf. Table XXII.) to the energy required for this dissociation rather than for the alternative: NaI + $h\nu \rightarrow$ Na($2P$) + I($2P_1$), with a metastable iodine atom as resultant. Whether or not the latter procsss can also occur at higher frequencies is as yet uncertain. In any case Terenin's observation that the sodium doublet 3302/3 Å is emitted instead of the D doublet when the wave-length of the exciting light falls to 1854 Å shows that a fourth region of selective absorption must begin about here associated with the photo-dissociation process: NaI + $h\nu \rightarrow$ Na($3P$) + I.

Hydrogen Halides.—Turning now to dipolar molecules with *atom* linkages, the hydrogen halides HCl, HBr, and HI may be taken as representative of this class. The infra-red rotation and vibration-rotation spectra of HCl and HBr which demonstrate the polar nature of these molecules have already been dealt with; the infra-red absorption of HI gas has not yet been examined. All three gases are completely transparent to visible light, but absorb again in the ultra-violet. The ultra-violet absorption spectra, first recorded by Coehn and Stuckardt (*Z. physikal. Chem.*, **91,** 722, 1916), have recently been subjected to more detailed examination by various workers. Leifson (*Astrophys. J.*, **63,** 73, 1926) finds that for HCl at atmospheric pressure all light below 235 $\mu\mu$ is absorbed. By reducing the pressure, the absorption is found to be compounded of three broad and strictly continuous bands with the approximate limits 215-185 μμ, 175-165 μμ, and 158-129 μμ, together with a fourth band which begins at 127 μμ. Tingey and Gerke (*J. Amer. Chem. Soc.*, **48**, 1838, 1926) have examined the absorption of HBr and HI from the violet down to 200 μμ and have fixed the long wave limits of absorption at 264 μμ for HBr and 332 μμ for HI. These limits are in good agreement with those found by Coehn and Stuckardt which were 265 μμ for HBr and 334 μμ for HI. The absorption spectrum of neither gas shows any trace of a discontinuous band system preceding the long wave limit, and the continuous absorption region from this into the far ultra-violet is in both cases without maxima. At the long wave limit there is a fairly sharp transition (within about 30 Å) from apparently complete absorption to apparently complete transmission. Variation of the pressure from 0·01 to 2 atmospheres or of the temperature from 25° to 400° has no influence on the general nature of the spectrum or on the position of its long wave limit. The continuous nature of the absorption spectrum of HI in the region 300-230 μμ has been independently verified by Bonhoeffer and Steiner (*Z. physikal. Chem.*, **122**, 287, 1926).

In so far as these spectra are strictly continuous, they resemble the absorption spectra of the alkali metal halides previously dealt with. For both cases, it would appear that every absorbed frequency effects the optical dissociation of the molecule—a result which suggests that the excited molecule as such has no separate existence. This conclusion is supported by the fact that no band emission spectra have ever been observed for the hydrogen halides or for the alkali metal halides.

The hypothesis of primary dissociation of the hydrogen halides which is suggested by the nature of their absorption spectra receives independent support from (*a*) Bonhoeffer and Farkas' observation (*Z. physikal. Chem.*, **132**, 235, 1928) that no perceptible fluorescence is emitted by hydrogen iodide at low pressures when strongly illuminated with the 2537 Å line which it absorbs; (*b*) Lewis' result (*J. Physical Chem.*, **32**, 270, 1928), confirmed by Bonhoeffer and Farkas, that the quantum yield of the photochemical decomposition of HI is independent of the pressure. The very marked adsorption of hydrogen atoms on the walls of the containing vessel, observed by Bonhoeffer and Farkas to occur when hydrogen iodide is illuminated with the mercury arc, does not of itself prove primary dissociation of the molecule, but only shows that H atoms appear in some stage of the photochemical process.

For the hydrogen halide molecules the possibility of optical dissociation into ions by absorption in the spectral region under consideration can at once be ruled out, since the heats of ionisation of the molecules (into H^+ and X^-) are of the order 300,000 calories, which would correspond to absorption below 100 μμ. The dissociation products must therefore be neutral atoms. The possibility of an activated hydrogen atom as resultant can also be discarded immediately, since the lowest excitation energy of this atom (10·16 volts or 230,000 calories) is of itself much greater than the total energy supplied optically. Accordingly there remain the two possibilities

$$\mathrm{HX} \rightarrow \mathrm{H} + \mathrm{X} \quad . \quad . \quad . \quad . \tag{1}$$

and

$$\mathrm{HX} \rightarrow \mathrm{H} + \mathrm{X}^* \quad . \quad . \quad . \quad . \tag{2}$$

We have seen that in the case of the alkali metal halides, which are ionic, both the corresponding processes are allowed in theory and confirmed by the observation of two regions of selective absorption, spectrally separated by the correct amount. For non-ionic molecules, however, theory suggests that process (2) should be the lowest stage of optical dissociation and that (1) should not occur. In agreement with this there is obtained for HBr and HI a single region of selective absorption,† which Franck and co-workers therefore associate with the optical dissociation of the hydrogen halide molecule into a normal hydrogen atom and a metastable halogen atom. It is important, of course, for the validity of this conclusion that the minimum available energy E for the photo-process, as calculated from the long wave limit λ of continuous absorption, should equal or exceed the requisite energy E_2. This condition is certainly fulfilled in the cases of HCl and HBr (cf. Table XXV). In the case of HI, the minimum available energy E seems to be slightly less than E_2 as calculated from the thermal heat of dissociation E_1 of HI into normal atoms and the Turner term difference $(2P_2 - 2P_1)$. The slight deficiency is probably only apparent, however, and due to inaccuracies in the values of λ and E_1, both of which may be in error by a few per cent.

TABLE XXV.

	Long Wave Absorption Limit λ $(\mu\mu)$.	E (kilocal.).	E_1 (kilocal.).	$(2P_2 - 2P_1)$ (kilocal.).	$E_2 = E_1 + (2P_2 - 2P_1)$ (kilocal.).
HCl . .	215	132	101	2·5	103·5
HBr . .	264	108	84·5	10·5	95
HI . .	332	86	69	21·5	90·5

The decompositions of HBr and HI by ultra-violet light happen to be two cases in which the relation between the number of quanta absorbed and the photochemical yield is specially simple. The stoichiometric result of the reaction in either case is

$$2\mathrm{HX} \rightarrow \mathrm{H}_2 + \mathrm{X}_2,$$

and the measurements of various workers show that, whatever the experimental conditions (as regards wave-length of the exciting radiation, state of aggregation of the halide, pressure, temperature, etc.) the quantum yield is always two, that is, two molecules of the halide are dissociated per quantum of radiant energy absorbed. This quantum yield is capable of two alternative explanations. Either the absorbing HX molecule is primarily dissociated into atoms, subsequent to which the resultant H atom decomposes a second HX molecule by thermal reaction, or the absorbing HX molecule is not primarily dissociated but only activated, and, by its collision with another unexcited HX molecule, a double decomposition into molecular hydrogen and halogen takes place. A choice between these two mechanisms in favour of the first is now possible, partly on the optical evidence dealt with above, partly on the observation of the independence of quantum yield upon the pressure already referred to. The alternative mechanism is briefly discussed in Chapter VIII.

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† The case of HCl which apparently exhibits a number of broad regions of selective absorption requires further consideration.

Silver Halides.—In concluding this Section we may refer briefly to some recent observations of Franck and Kuhn (*Z. Physik*, **43,** 164; **44,** 607, 1927) which point to the fact that the type of binding in the silver halide (AgCl, AgBr, AgI) molecules in the vapour state must be non-ionic, that is to say, these molecules resemble those of the hydrogen halides rather than those of the alkali metal halides. The evidence given by Franck and Kuhn in support of this thesis derives partly from the fact that the vapours of AgBr and AgI have, like the corresponding hydrogen compounds, only one region of continuous selective absorption in the ultra-violet (corresponding, in all probability, to the photo-dissociation $AgX \rightarrow Ag + X^*$), partly from the fact that the strength of binding of the normal vapour molecule, as deduced from the spacings of its fluorescence bands, is much less than would be anticipated for a molecule of ionic structure. Further, the heat of dissociation of the normal AgI vapour molecule, as obtained by extrapolation of the normal vibrational sub-levels to zero spacing, agrees roughly with the thermally calculated heat of the reaction $AgI \rightarrow Ag + I$, but is much smaller than the heat of the process of ionisation $AgI \rightarrow Ag^+ + I^-$. In the vapour state at least, then, the silver halides are atom compounds. On the other hand, silver chloride and silver bromide both form definitely ionic lattices in the crystalline state of aggregation. (The type of binding in solid silver iodide is not so certain. The β-modification, stable at ordinary temperatures, appears to be an atomic linkage, whereas the α-modification, stable above 145° C., is probably ionic.) Accordingly, we appear to have in the silver halides examples of compounds which with suitable variation in the conditions (state of aggregation, temperature) can pass from the atomic to the ionic type of binding, and *vice versa*. Certain other physical properties of these salts, such as their colour change and the anomalous dependence of their electrical conductivity in the liquid state on temperature, also suggest that the ionic binding, which is stable at low temperatures, passes over into the atomic as the temperature is increased.

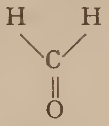
ABSORPTION SPECTRA OF POLYATOMIC GASES AND VAPOURS. PREDISSOCIATION SPECTRA.

A large amount of experimental work has been done within recent years on the absorption spectra of the gases and vapours of polyatomic substances, in especial of organic compounds. Such spectra are naturally expected to be much more complex than those of diatomic substances, both as regards the structure of their band systems and also as regards the fine structure of the individual bands themselves. For the diatomic molecule with a single principal moment of inertia, we have seen that the fine lines constituting the individual band are represented by parabolic functions of a single integral variable m. Should the molecule, however, possess two principal moments of inertia, as in the symmetrical top model, each stationary state will involve two independent rotational quantum numbers (cf. equation (17)), and the totality of lines in the individual band should therefore fall into two distinct groups (two R, two P, and two Q branches). From the analysis of such a band, which though difficult need not be impossible, the moments of inertia of the molecule and something of its spatial configuration may be deduced. The case of formaldehyde cited below provides an example. In the general case where the absorbing molecule is asymmetrical, possessing three unequal moments of inertia, the complexity of the individual bands may well be such as to baffle analysis.

As regards the electronic band group for the molecule which has several degrees of freedom of vibration, theory suggests that this should be represented by a generalisation of the group function $\nu = f''(p'') - f'(p')$ which applies to the case of the diatomic molecules, viz.

$$\nu = f_1''(p_1'') - f_1'(p_1') + f_2''(p_2'') - f_2'(p_2') + \ldots,$$

where p_1', p_2' . . . and p_1'', p_2'' . . . are the vibrational quantum numbers in the lower and upper states of excitation, and the f's are, to a first approximation, quadratic functions of the p's. Possibly also, combination terms—terms in $p_1'p_2'$, $p_1''p_2''$, etc.—would have to be included to take account of the mutual actions of the vibrating parts of the molecule. Clearly the analysis of such complex band systems would be impossible in practice without such adventitious help as might be afforded by intensity gradations in the bands, or by the spectral segregation of various bands into obvious sequences, or by the occurrence of practically arithmetic progressions of bands due to one or more of the above f functions being specially simple. Although the first stages of analysis have indeed been effected in numerous cases by such means as these, it must nevertheless be confessed that the analysis has seldom been carried to the point where the true vibrational quantum numbers may be ascribed to each band—a necessary preliminary to the accurate estimation of the natural vibration frequencies of the absorbing molecule. As an example of one of the few cases of a band system which has been analysed in fair detail, we may take the ultra-violet band absorption spectrum of formaldehyde vapour, recently investigated by Henri and Schou (*Z. Physik*, **49,** 774, 1928). This spectrum consists of thirty-five to forty absorption bands lying between 370 and 250 $\mu\mu$ which form eleven natural sub-groups, each containing three or four bands. The individual bands of the first seven (the longer wave-length) sub-groups reveal under dispersion a complex fine structure of absorption lines corresponding to the quantisation of the rotational motion of the formaldehyde molecule. A detailed analysis shows that the fine structure of each band involves a doubly quantised rotation of the molecule, such as would be obtained in the symmetrical top model mentioned above. On this basis, the two principal moments of inertia of the normal molecule can be calculated from the optical data. The moment of inertia round the symmetry axis, which would be the $C = O$ axis of the formaldehyde molecule, is $I = 1{\cdot}38 \times 10^{-40}$ c.g.s. units; that round an axis perpendicular to this is $K = 23 \times 10^{-40}$ c.g.s. units. From these values, Henri and Schou construct a plane model, viz.



of the formaldehyde molecule with the following dimensions :—

$$H - H = 1{\cdot}38 \times 10^{-8},\ C - O = 1{\cdot}09 \times 10^{-8},\ C - H = 1{\cdot}3 \times 10^{-8}\,\text{cm.}$$

The different sub-groups of bands in the spectrum are primarily of the nature of sequences, that is, they correspond, passing from longer to shorter wave-lengths, to an ever-increasing extent of vibrational excitation involved in the act of absorption. Quite a number of these bands may be represented by the ordinary group formula characteristic of the band spectra of molecules with a single degree of freedom of vibration, viz.

$$\nu = \nu_0 - \beta' p' + \beta'' p'' + \gamma' p'^2 - \gamma'' p''^2$$

or

$$\nu = \nu_0 + (p'' - p')\beta'' + p'(\beta'' - \beta') + \gamma' p'^2 - \gamma'' p''^2,$$

with $\beta' = 1572{\cdot}3$, $\beta'' = 1231{\cdot}3$, $\gamma' = 0$, $\gamma'' = 8$, and with $p'' - p' = 1, 2, 3, 4 \ldots$ for the different sub-groups or sequences. Several of the bands, however, and among these the band of greatest intensity in each sub-group, do not fit into this scheme, and Henri and Schou have therefore made use of a more elaborate group formula involving two degrees of freedom of vibration of the molecule. The β' and β'' of the additional vibration are given as 441 and 398 cm.$^{-1}$ respectively. The anomalous bands are regarded as deriving from the simultaneous excitation of both degrees of freedom of vibration of the molecule. For various reasons which we need not detail, the stronger vibration

($\beta' = 1572$ cm.$^{-1}$) is associated with the C = O linkage, the weaker vibration ($\beta' = 441$ cm.$^{-1}$) with the mutual vibration of the hydrogen atoms in the molecule.

State of Predissociation of Molecules.—It will be convenient here to introduce with the case of formaldehyde the concept of "predissociation" which has emerged in recent years from the work on absorption spectra of Henri and co-workers. As stated above, all the bands in the first seven sub-groups ($\lambda = 370 - 280\ \mu\mu$) in the spectrum of formaldehyde vapour exhibit under high dispersion a duplex fine structure corresponding to a doubly quantised rotation of the molecule about two principal axes of rotation I and K. The main band ($\lambda = 275\ \mu\mu$) of the next sub-group (the eighth) also possesses a rotational fine structure, but this differs in character from that of the preceding bands, in that no discrete fine lines associated with the rotation of the molecule round the K axis are any longer observed. In the absence of these, the fine lines which are actually observed and which are those associated with rotation of the molecule round the I axis are considerably broadened. For the main band of the next sub-group ($\lambda = 267\ \mu\mu$), even the fine structure associated with rotation round the I axis has disappeared; the absorption is now continuous over the whole width of the band (about 4 Å), although as regards its internal distribution of intensity the band resembles that at 275 $\mu\mu$ with the broad lines of the latter still further broadened so as to overlap. The remaining observed bands of the system up to 250 $\mu\mu$ are all strictly continuous.

In preceding Sections, we have associated *broad* regions of strictly continuous absorption on the part of gases and vapours with the occurrence of an optical dissociation of the absorbing molecule into its component parts. Such dissociation, however, would at first sight appear to be excluded in the case of any of the above described bands of formaldehyde vapour, since (*a*) the bands though continuous are still narrow and discrete, and (*b*) they fall as regards their spectral positions into the same group or system as the longer wave-length discontinuous bands. Rather, the fading out of fine structure in the shorter wave-length members of the band group seems to imply that beyond some limiting extent of excitation (electronic + vibrational) the rotational motion of the excited molecule ceases to be quantised, although the molecule is not yet dissociated and the vibrational motion of its parts is still governed by quantum laws. The state of the molecule under these conditions is termed by Henri a state of "predissociation." From the characteristics of the absorption spectra of a large number of substances (chiefly organic) in the vapour state, Henri has concluded that this phenomenon of predissociation is by no means of exceptional but rather of very general occurrence. We quote from the paper referred to above. "When one examines the structure of a series of [absorption] bands corresponding to the same electronic excitation and progressively increasing vibrational excitation, it is found that beyond a certain limit the rotational fine structure of the bands disappears and only the vibrational states are quantised. In certain cases, as S_2, NO_2, SO_2, the change from the spectrum with fine structure to the spectrum with continuous bands is quite sudden, the limit permitting of estimation to a few tenths of an Ångström; in other cases the transition occurs quite gradually [as in the case of formaldehyde above]. The number of successive vibrational states with quantised rotation (fine structure) which a molecule possesses before the state of predissociation appears, differs greatly from molecule to molecule. . . . Investigation of the properties of the molecule in this state of predissociation has shown that it is chemically reactive, that the fluorescence excited by illumination with the corresponding radiation is very feeble, and that the vibrational frequency of the atoms is smaller [than in the normal state], i.e. that the separation of the atoms in the molecule is increased. It is therefore a state intermediate between that of the stable molecule and that of the dissociated molecule."

The "predissociation spectrum" of sulphur is of special interest since in this case we are dealing with absorption of radiation by admittedly diatomic molecules. The ultra-violet absorption bands of sulphur vapour were originally classified by Henri and Teves (*Compt. rend.*, **179,** 1156, 1924) as belonging to four distinct systems, i.e., corresponding to four different extents of electronic excitation of the sulphur (S_2) molecule. The more recent analysis of Rosen (*Z. Physik*, **43,** 69, 1927) has, however, shown that all the bands belong to one and the same system represented by the equation

$$\nu = 32{,}140 + (424{\cdot}4\ p'' - 2{\cdot}7\ p''^2) - (724{\cdot}5\ p' - 2{\cdot}91\ p'^2).$$

The important result of Henri and Teves' experimental work, however, was to show that a sharp break in the nature of the absorption bands takes place at 2794 Å. All bands of wave-length greater than this possess rotational fine structure, all bands of smaller wave-length are strictly continuous. The breadth of these continuous bands increases from one or two to about fifteen Ångström units as we pass towards the ultra-violet. From Rosen's analysis, these "predissociation bands" of sulphur vapour (which, it must be emphasised, belong to the same system as the longer wave-length bands) are all characterised by small values of p' and large values of p'', that is, they correspond to a large increase in the vibrational energy of the absorbing molecule. The first predissociation band associated with the vibrationless molecule ($p' = 0$) occurs at $\lambda = 279\ \mu\mu$ and is that for which $p'' = 9$. It cannot, of course, be allowed that the so excited molecule is near to optical dissociation in the sense that we have hitherto understood by this term, since the region of continuous absorption which is appended to the convergence limit of the $p' = 0$ progression and which corresponds to the true optical dissociation of the sulphur molecule into a normal and an excited atom does not start before $250\ \mu\mu$ (cf. p. 224). On the other hand, the sulphur molecule which has absorbed the frequency of a predissociation band does in all probability possess sufficient excess energy (electronic, vibrational, rotational, and translational) to permit of its dissociation into two normal sulphur atoms *if a favourable redistribution of this total excess energy could be achieved by any means.* Rosen's lower estimate for the heat of dissociation of the molecule into normal atoms is 107,000 calories (cf. p. 225), while the quantum absorbed by the vibrationless molecule in the first predissociation band at 279 $\mu\mu$ gives an amount of energy—electronic *plus* vibrational—of 102,500 calories. Remembering that the absorption measurements refer to a temperature of 450° to 650° C., it is clear that the additional 4500 calories necessary (energetically) for dissociation may be resident in the absorbing molecule as translational and rotational energy. This fact is significant when taken in conjunction with the general result, established in numerous cases by Henri and co-workers, that with increasing temperature of the absorbing vapour the predissociation limit is displaced towards longer wave-lengths. Indeed, this dependence of the predissociation limit on temperature would appear of necessity to imply that the peculiar nature of the so-called predissociation bands derives from some sort of energy adjustment in the molecule subsequent to the act of absorption.

What is the nature of this energy adjustment, and how is it effected ? Up till quite recently, it has been a commonly accepted idea that such a redistribution of energy as above implied could not occur spontaneously in the isolated molecule, but that to effect it a collision with another molecule would be necessary. An appeal to molecular collisions is, however, useless to explain the peculiar nature of predissociation bands. On the one hand, their lack of rotational fine structure persists down to very low pressures of the absorbing gas, such that the time between consecutive collisions becomes much greater than the life period of 10^{-7} to 10^{-8} seconds which is usually associated with the excited state ; on the other hand, it is difficult to see how molecular collisions, taking place per 10^{-10} sec. at ordinary pressures, could cause any appreciable lack of definition in the quantisation of the rotational motion of the excited molecule which has a natural period of the order of 10^{-12} sec. The fact that the rotation of the molecule which has absorbed a predissociation band is not quantised while its vibrational motion is quantised must mean that something catastrophic happens to the excited molecule within a time interval which is greater than the natural period of the vibration, but of the order of magnitude of the natural period of the rotation, namely 10^{-12} sec. This at once rules out not only molecular collisions but also any effect of the nature of a fluorescence of the absorbed energy, since the normal life of an excited molecule which fluoresces is known to be of the order of 10^{-7} to 10^{-8} sec. We seem, therefore, to be forced to the view that it is dissociation which follows the act of absorption of a predissociation band, and that the necessary energy adjustment within the molecule—the localising of its total excess energy in a single degree of freedom of vibration—is spontaneous in character.

Fortunately, such a process is not in disaccord with the principles of the new quantum mechanics, and moreover the occurrence of an essentially analogous process has recently been established in the case of the atom. In what is known as the Auger process, a quantum jump takes place *spontaneously* in the atom without the simultaneous emission of radiation. The excited atom, instead of disposing of its excess energy by the emission of a light quantum, utilises this energy to eject an electron with corresponding velocity. If, for example, we have an atom which is ionised in the K shell, the normal event is the filling of this shell at the expense of some outer shell with the emission of a line of the element's K series. Instead of this emission, however, it sometimes happens that the energy rendered available by the filling of the K shell is used to eject another electron out of the atom from one of the other shells. Here we have the spontaneous transformation of energy originally associated with certain other parts of the atom into translatory energy of the two separating parts—the atom residue and the ejected electron. In much the same way, we can imagine the utilisation of all the available excess energy of an excited molecule to effect its separation into atoms.

Strong evidence in support of this interpretation of predissociation spectra has recently been afforded by certain observations of Bonhoeffer and Farkas (*Z. physikal. Chem.*, **134,** 337, 1928) with ammonia vapour. The absorption spectrum of this vapour in the short wave ultra-violet had been previously examined by Leifson (*Astrophys. J.*, **63,** 73, 1926). This spectrum consists of a number of regularly spaced bands extending from about 220 to 160 $\mu\mu$ which almost certainly form a Deslandres second progression, that is, they all derive from the same initial state of the absorbing molecule. The bands exhibit no internal structure of rotation lines, however, but are perfectly continuous. The absence of fine structure is specially noteworthy in the present instance, since the NH_3 molecule has a very small moment of inertia, and therefore the spacing of the individual rotation lines of each band should be very large. A large spacing is in fact found in the infra-red (rotation-vibration) bands of ammonia which are perfectly normal in character, but a degree of optical resolution which should easily permit of the detection of a similar fine structure in the ultra-violet bands is without result. The ammonia bands must therefore be regarded as predissociation bands.

If the excited molecule of ammonia has an unnaturally short period of existence, as our interpretation of such bands demands, it should then be impossible or at least very difficult to obtain a band emission spectrum of ammonia. This has been tested by Bonhoeffer and Farkas in two ways. It was attempted to obtain the ammonia bands in fluorescence. No trace of fluorescence was obtained, however, even when the vapour was illuminated at such low pressures (less than 0·1 mm.) as are usually favourable for the occurrence of this phenomenon. It may be recalled that this negative result is in agreement with the general thesis of Henri and co-workers that good capacity for fluorescence goes hand in hand with sharp line absorption. When a substance exhibits both normal and predissociation absorption bands in different spectral regions, it can readily be made to fluoresce by illumination with radiation of the first region, but less readily or not at all by illumination with radiation of the predissociation region. It was next attempted to obtain an emission spectrum of ammonia by exciting the molecule by electronic collisions in a discharge tube, but again a negative result was obtained. In this case, as in the attempt to excite fluorescence, there is no reason to suspect that excitation of the molecule does not occur. The important point is that the excited molecule does not under the most favourable conditions dispose of its excess energy by emission. From this we are forced to conclude that the excited molecule decomposes before it has time to emit, and, under the low pressures obtaining in these experiments, the dissociation cannot be other than spontaneous.

Further evidence in support of this view is adduced by Bonhoeffer and Farkas from the circumstance that the extent of photochemical decomposition of ammonia into nitrogen and hydrogen, when illuminated by light of the predissociation region, remains appreciable even when the pressure of the system is reduced to 0·001 mm. There are two different possible mechanisms for this photo-reaction, depending upon whether the primary light process is assumed to be an excitation or a dissociation of the absorbing molecule. If it be assumed, however, that the molecule of ammonia is merely excited by light absorption and must then suffer a collision with another molecule for reaction to occur, it is very difficult to see how an appreciable photochemical yield could be obtained at such a low pressure as that mentioned above. At this pressure the mean free path of the excited molecule would be greater than the dimensions of the containing vessel, so that the molecule would collide more frequently with the walls than with other molecules. Even if wall collisions did not deactivate the excited molecule, it would then be necessary to assume an impossibly large value for its natural life period, viz. about 10^{-4} sec., to account for the observed photochemical yield. On the other hand, the reaction mechanism which postulates primary dissociation of the absorbing molecule of ammonia—or, more correctly expressed, spontaneous decomposition of the ammonia subsequent to its primary excitation—avoids these difficulties and makes intelligible the experimental result of appreciable photo-decomposition even at the lowest pressures.

In conclusion, it may be well to recapitulate and to emphasise the distinction which is drawn between normal band absorption, predissociation or diffuse band absorption, and continuous absorption by gases and vapours. From normal band absorption there results an excited molecule which, if isolated, must inevitably dispose of its excess energy by emission as fluorescence. As we shall see in the following Chapter, such excited molecules have a normal life period of the order 10^{-7} to 10^{-8} sec. If within its normal life period the excited molecule suffers a collision, it may retain all its internal energy (elastic collision), or it may dispose of all or part of this energy by transfer to the colliding partner, or its internal energy may suffer a redistribution among its various degrees of freedom without appreciable transfer. In the last event, dissociation of the molecule may occur. By absorption within a predissociation band the primary product is again an excited molecule, but of exceedingly short life—a life comparable with the period of rotation of the molecule. Before the molecule can fluoresce or collide with its neighbours a spontaneous redistribution of energy appears to take place within it which results in its dissociation. As regards the details of this internal energy adjustment, however, or the conditions necessary for its occurrence nothing definite can be said. It is a commonplace that many molecules can absorb energy far in excess of their energy of dissociation without such spontaneous dissociation taking place, and this is referred to the circumstance that all the absorbed energy is not located in the degree of freedom of vibration pertinent to dissociation, yet this is also the case with the molecule which has absorbed a predissociation band. The possibility of occurrence of the internal re-arrangement of energy seems to be greatest in complex molecules, since predissociation spectra are confined with a few exceptions to organic bodies. Finally, the fate of the molecule which absorbs in a broad continuous region—a region which may or may not be appended to an observed band system—is immediate dissociation. The characteristic of such absorption is that the increase in vibrational energy which is coupled with the main electronic excitation suffices in itself to effect the separation of the molecule into its parts. The band structure which would be observed in default of this condition disappears, since there is now an infinite continuum of possible final states of the absorbing system corresponding to the continuously variable translatory energy of the separating parts.

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CHAPTER V.

FLUORESCENCE.

The various elementary processes involved in sub-atomic and molecular physics are so intimately connected with one another that it would have been difficult and indeed inadvisable to avoid some previous reference to the type of phenomenon which forms the subject matter of the present Chapter. We now proceed to give a more detailed account of the photoluminescence of matter in the gaseous and liquid states of aggregation, paying special regard to (*a*) the relationship which exists between the exciting (absorption) spectrum and the luminescence (emission) spectrum of each system concerned, and (*b*) the conditions which favour or militate against the re-emission by matter of the radiant energy which it absorbs. In so doing, we shall find the opportunity to discuss certain subsidiary effects of the action of light on matter which are important in relation to photochemical theory.

In confining discussion to gaseous and liquid systems we necessarily restrict ourselves to those photo-processes which are included under the general heading of fluorescence, and we exclude from consideration the many striking afterglow phenomena formally described as phosphorescence which are associated with the solid state of aggregation and especially with solid solutions. In *fluorescence* the process of emission of the absorbed radiant energy is of exceedingly short duration, a time interval of only $10^{-7} - 10^{-9}$ sec. elapsing between the instant of withdrawal of the exciting radiation and the practical cessation of the induced emission. In *phosphorescence* the process of emission is extended over easily measurable periods of time—for different substances and under different conditions, periods varying from a fraction of a second to several years. Properly speaking, however, it appears that the term phosphorescence should only be applied to the *after-glow* of the pre-illuminated solid or solid solution and not to the total emission during illumination, since in many cases it has been established that the latter emission is composite of two independent processes—the one a true momentary fluorescence, the other a phosphorescence which alone persists after the illumination is withdrawn. The momentary fluorescence and the after-glow can possibly be referred to different centres of excitation in the solid, " momentary " centres and " persistence " centres respectively. In gaseous and liquid systems (with certain exceptions) only momentary centres of excitation are active; in solid systems we may have both momentary and persistence centres, or persistence centres alone.

The two extremes of photoluminescence are represented by the resonance radiation of monatomic gases at low pressures and the phosphorescence of the alkaline earth phosphors of Lenard. In the first case, the elementary process of absorption involves the excitation of the practically isolated atom, and this within a period of about 10^{-8} sec. reverts spontaneously to its normal state with re-emission of radiation of the same frequency as it absorbed. On the other hand, the elementary processes concerned in the excitation of an alkaline earth phosphor are generally supposed to involve (*a*) the complete ejection of electrons from their binding in special parts of the complex crystal lattice, and (*b*) the re-capture by the ionised centre of an electron, either the initially ejected electron itself or another electron drawn from some part of the surroundings. The ease with which process (*b*) can be effected in the solid determines the intensity and the duration of the photoluminescence. Very considerable support to this mechanism of the excitation of the alkaline earth phosphors is afforded by the fact that the same radiation which causes the emission also produces a photoelectric conductivity in the solid crystal. It is not by any means certain, however, that a photoelectric process is always operative in the delayed re-emission of absorbed radiant energy by solid systems. For organic compounds, whether in the pure solid state or in solid solution, the region of activating wave-lengths which produces the phosphorescence of the solid is essentially the same as the region responsible for the fluorescence of the same substance in the vapour and liquid states, and the evidence is all against a photoelectric action of the absorbed radiation in the latter states. Furthermore, the photoluminescence of the pure solid at ordinary temperatures differs in no essential from that of the vapour or liquid, except in that it persists for definitely longer periods after the illumination is withdrawn. In respect of duration, then, the emission process is formally a phosphorescence, but in respect of its spectral characteristics it is best regarded as a "fluorescence of long duration." What may more properly be regarded as the phosphorescence of organic compounds is the after-glow spectrum of these substances which is developed in solid solution (solvent medium—alcohol, chlorobenzene, boric acid, sucrose, etc.) at very low temperatures, but even in this case the same region of absorption is concerned in the excitation of the after-glow spectrum as in the excitation of the fluorescence spectrum, although the after-glow spectrum is very different from, and much more complex than, the fluorescence spectrum. When in the latter part of the present Chapter occasional mention is made of the "fluorescence" of organic compounds in the solid state and in solid solution, it is to be understood that we are always referring to the emission obtained during the continuance of the exciting illumination, which emission, at ordinary temperatures, is always more or less comparable with the true fluorescence of the compounds concerned in the vapour or liquid states or in liquid solution. For a detailed account of photoluminescence phenomena in general, the reader is specially referred to Pringsheim's *Fluorescenz und Phosphorescenz im Lichte der Neueren Atomtheorie.*

RESONANCE RADIATION.

Optical resonance in the narrowest sense of the term implies the absorption of monochromatic radiation of a particular frequency by a substance and the re-emission of radiation of the same frequency and none other. In practice, examples of such pure resonance are few in number, and the reason for this is immediately clear when we consider the internal energy levels of atoms and molecules and their various possibilities of combination in emission and absorption. For pure resonance it is necessary that the excited state attained by the act of absorption should have no possibilities of combination in emission with any state other than the original. Molecules are accordingly excluded from the possibility of pure resonance by absorption in the near infra-red, visible, or ultra-violet, since, by reason of the compound character of their normal and excited energy levels, it follows that in any vibrational or electronic energy level attained by such absorption, the excited molecule has always more than one way of disposing of all or part of its acquired energy by spontaneous emission. There exists, of course, the comparatively unimportant (and as yet unrealised) eventuality of resonance by heteropolar molecules in the far infra-red, where the molecule having absorbed a frequency of its pure rotation spectrum could pass spontaneously by emission only to its original condition.

For atoms, the condition that the excited state reached by absorption should combine in emission with but one other state, and that the original, confines the phenomenon of pure resonance in practice to the elements of the first and second groups of the Periodic Classification and confines the resonance frequencies themselves to the first members $\nu = 1S - 2P$ of the Principal Series of these elements. These are the elements which are monatomic in the vapour state and for which the lowest internal energy level is represented by a singlet $1S$ term. Clearly, if the lowest energy level of an atom is represented not by a singlet S term but by a doublet P term, say $2^2P_{1,2}$, the excitation by absorption of either the normal (2^2P_1) atom or the metastable (2^2P_2) atom permits of at least two possibilities of spontaneous emission (cf. the fluorescence of thallium vapour, p. 251). With increasing multiplicity of the normal energy level the number of such possibilities is of course proportionately increased.

As regards the experimental conditions under which pure resonance can be excited in a monatomic vapour, the optimum yield of resonance can obviously only be expected if the excited atoms within their period of existence have no option other than that of spontaneous emission. For this reason, foreign gases must be excluded and the pressure of the vapour itself must be low. The normal life of the labile excited state of an atom is of the order 10^{-7} to 10^{-8} sec., while the average time between consecutive collisions in a gas at ordinary pressures is about 10^{-10} sec. Accordingly, working pressures of considerably less than a millimetre of mercury are necessary to avoid the possibility of deactivation of the excited atoms by collision. The actual dependence of the yield and purity of resonance upon pressure and upon the presence of foreign gases is naturally of great importance in the general theory of photo-processes. Before dealing with this, however, we will first consider particular examples of resonance in monatomic vapours under conditions which preclude the appearance of collisional effects.

Of the metal vapours which may be expected to yield pure resonance radiation, only the cases of sodium and mercury have as yet been investigated in detail, although the resonance of lithium, zinc, and cadmium has also been observed recently. A glance at the energy diagram of the sodium atom (cf. p. 125) shows that in this case there should be two resonance frequencies—the two lines which are the components of the doublet $\nu = 1S - 2P_{1, 2}$ in the arc spectrum of sodium. Dunoyer (*Le Radium*, **10,** 400, 1913) found that when carefully purified sodium is vaporised in an evacuated bulb at temperatures somewhat above 100° C. and the vapour illuminated with a narrow directed beam of light from a sodium flame or arc, resonance is obtained. The sodium vapour throughout the whole path of the incident ray emits a soft yellow glow which can only be ascribed to the emission in all directions of the D lines by excited atoms in the path of the ray. For transverse observation, the path and cross-section of the incident ray are sharply defined by the spatial limits of the re-emission in much the same way as the path and cross-section of a beam of sunlight are made clear for transverse observation through scattering of the light by dust particles. Both the D lines appear in the resonance radiation if they are also present in the exciting light. If, however, the incident radiation contains only one component of the doublet, that component alone is present in the emission.

The vapour pressure of sodium at 100° C. is only about 10^{-7} mm., and at such a pressure an incident beam of sodium light is very little decreased in intensity in passing through a considerable depth of vapour. If, however, the temperature be increased, and thereby also the saturation vapour pressure of the sodium within the bulb or " resonance lamp " as it is called, the absorption is increased and the distance of penetration of the incident beam decreased. On this account the resonance emission is found with increasing temperature to become more intense and at the same time more and more localised near the point of entry of the exciting beam. Simultaneously the boundaries of the zone of resonance emission become less sharply defined, that is, a diffuse emission of sodium light is observed from regions which definitely lie outside the cross-section of the primary beam. This diffuse emission cannot originate from atoms which have been excited on the periphery of the incident beam and then escape into the body of the vapour before emitting. The average life of the excited atoms is about 10^{-8} sec., and their average linear velocity under the experimental conditions is less than 10^5 cm./sec., so that a very small fraction of the atoms excited in the path of the incident beam can travel a distance greater than 10^{-3} cm. before spontaneously emitting. The most reasonable explanation of this diffuse emission which comes from outside the cross-sectional limits of the incident beam is that it is of a secondary nature, arising from progressive absorption and re-emission of the primary resonance radiation by successive outer zones of vapour.

With sodium vapour in the resonance lamp at the saturation pressure corresponding to 250° C., which is about 0·01 mm., the distance of penetration of the incident beam is only about 6 mm. and the region of emission of resonance radiation is correspondingly limited. At 300° C. ($p = 0{\cdot}025$ mm.) all the incident radiation is absorbed within a fraction of a millimetre, and the "volume resonance" is transformed into "surface resonance." It is as if an impenetrable surface of sodium vapour were opposed to the incident beam and scattered it outwards in all directions, just as the surface of paper scatters white light in all directions. The true explanation of surface resonance is that the incident beam is completely absorbed within a very thin layer of vapour and is re-emitted as resonance radiation in all directions, but that part of this primary resonance radiation which attempts to penetrate further into the vapour is reabsorbed by the next layer, again emitted in all directions as secondary resonance, and so on, the net result being that the whole absorbed radiant energy reappears as primary, secondary, tertiary, etc. resonance radiation emitted uniformly outwards in all directions from the illuminated surface. With reference to the efficacy of the illuminating radiation in producing resonance, whether of the volume or of the surface type, it must be noted that this should depend primarily upon the purity of the exciting light. In illuminating a resonance lamp containing sodium vapour with the light of an ordinary sodium flame, each of the D lines in the exciting beam has a width at least as great as the Doppler width corresponding to the temperature of the flame, and therefore only a narrow middle portion of each broad line will be absorbed by the vapour which is at a much lower temperature. The width absorbed should, in fact, be equal to the Doppler width at this temperature (provided other broadening effects due to electric or magnetic fields, or to the proximity of other atoms or molecules, are absent), and the resonance lines emitted should be equally narrow. In agreement with this, the half-width of the D_2 line in the surface resonance of sodium vapour at 300° C. has been estimated by Dunoyer and Wood and also by Strutt to be about 0·02 Å, which is equal to the half-width calculated from the Doppler broadening at this temperature of an infinitely narrow line of the same wave-length.

In order to make a legitimate comparison of the input of radiant energy with the output, Dunoyer has adopted the simple expedient of using the resonance radiation from one resonance lamp to excite resonance in another resonance lamp. Distinguishing the lamps as first and second respectively, a strong surface resonance is induced in the first, which is maintained at 300° C., by illumination with the ordinary sodium flame. When part of this surface resonance is directed on to the surface of the second lamp, maintained at the same temperature, the illuminated surface appears just as bright as does a white surface placed in the same position (the white surface diffusely reflects practically 100 per cent. of the incident radiation). This is not the case, however, if the second lamp is illuminated directly with the light of an ordinary sodium flame. It follows, of course, that both the absorption and the re-emission are complete when sodium vapour under the specified conditions is illuminated with resonance radiation of its own quality, and from this it may be further inferred that, even when the illuminating line is too broad to be completely absorbed, all the radiation which *is* absorbed will be re-emitted by the vapour.

Lithium is the only other alkali metal for which a pure resonance emission has so far been obtained. Bogros (*Compt. rend.*, **183,** 124, 1926) finds that lithium vapour saturated at 540° C. re-emits the first line 6708 Å of the Principal Series.

The mercury atom possesses two distinct possibilities of pure resonance, corresponding respectively to the reciprocal processes

$$\mathrm{Hg}(1^1S_0) + 2536{\cdot}7\ \text{Å} \rightleftharpoons \mathrm{Hg}(2^3P_1)$$

and

$$\mathrm{Hg}(1^1S_0) + 1849\ \text{Å} \rightleftharpoons \mathrm{Hg}(2^1P_1).$$

Little need be said concerning the second of these. The 1849 Å resonance has indeed been observed by Rump (*Z. Physik*, **31,** 901, 1925), but the wave-length in question lies in the region of strong absorption by atmospheric oxygen, so that conditions are not very suitable for its detailed study. The 2536·7 Å resonance was first noted by Wood in 1909, and has since been very extensively investigated by him and other workers. The details of the resonance phenomena are very similar to those of the sodium D resonance. The mercury vapour is illuminated in a quartz tube with the light of a quartz mercury lamp. As with sodium, the volume resonance is detectable, though faint, at very low pressures of the order of 10^{-7} mm. (the saturation pressure of Hg at − 50° C.). With increasing pressure (temperature) it becomes more and more intense, and gradually the volume resonance passes over into surface resonance. For a given intensity of illumination this surface resonance is brightest at about 100° C. ($p_{\mathrm{Hg}} = 0{\cdot}28$ mm.). With a further increase of temperature, the intensity of re-emission falls off and at 270° C. the resonance is scarcely perceptible. This low efficiency of resonance at higher vapour pressures is attributable partly to deactivation of the excited mercury atoms by collision with other mercury atoms, partly to the fact that at high pressures the illuminated surface of mercury vapour begins to acquire the power of regular (optical) reflection of the 2536·7 Å line and neighbouring wave-lengths. As mentioned above, the excitation of the mercury resonance line is usually effected by illumination with a quartz mercury lamp, but a reasonable intensity of resonance in moderately cool vapour can only be obtained provided self-reversal of the 2536·7 Å line, that is the complete or nearly complete absorption within the lamp itself of the central part of the line, is avoided, since this central part alone is effective in producing resonance radiation. This difficulty is overcome either by running the mercury lamp at low pressure by external cooling of the electrodes or by bending the middle of the arc into contact with the exit wall by means of a strong magnetic field.

Zinc and cadmium should be analogous to mercury in possessing two possibilities of pure resonance. In agreement with this, zinc vapour saturated at 280° C. ($p_{Zn} = 5 \times 10^{-4}$ mm.) emits as resonance the lines 3076 ($1^1S_0 - 2^3P_1$) and 2139 ($1^1S_0 - 2^1P_1$) when illuminated with the light of a zinc vacuum arc, and cadmium vapour emits the lines 3261 ($1^1S_0 - 2^3P_1$) and 2289 ($1^1S_0 - 2^1P_1$) under corresponding conditions.

Dealing still with monatomic vapours at low pressures, we may now consider one or two cases of the emission, under monochromatic illumination, of frequencies which differ from the exciting frequency. An example of such is found in Strutt's observation (*Nature*, **95,** 285, 1915; *Proc. Roy. Soc.*, **96**A, 272, 1919) that when sodium vapour is illuminated with the second doublet (3302/3 Å) of the Principal Series, the fluorescent emission of the vapour always contains the two D lines, however carefully these lines are excluded from the incident beam. Strutt further observed that if the exciting radiation contains only one component of the ultra-violet doublet, viz. the line 3303 Å, *both* D lines are nevertheless present in the fluorescence. There are two possible explanations of these results. The energy diagram of sodium (p. 125) shows that the atom when excited to one of the 3^2P levels may revert spontaneously to the normal 1^2S level either in one step (pure resonance) or in three consecutive steps, viz. $3^2P \rightarrow 2^2S$ (or 3^2D) $\rightarrow 2^2P \rightarrow 1^2S$. In the latter event, of course, one or other of the D lines would be emitted together with lines in the infra-red which would escape observation, and since no restriction is imposed upon the excited atom in its deactivation by stages to prefer one of the 2^2P levels to the other, the presence of both D lines in the fluorescence is not surprising. An alternative explanation of the emission of the D lines lies in deactivation of the 3^2P atom in *two* consecutive stages, viz. $3^2P \rightarrow 2^2P \rightarrow 1^2S$, the first of these, which is forbidden as a spontaneous process, occurring by collisions of the excited 3^2P atoms with other sodium atoms. It is probable that under Strutt's conditions of observation, both modes of transit from the 3^2P state to the 2^2P state—by double emission and by collision—are effective.

The fluorescent emission of thallium vapour, as studied by Terenin (*Z. Physik*, **31,** 26, 1925; **37,** 98, 1926), provides a slightly different example of the type of phenomenon under discussion. The normal and metastable energy levels of the thallium atom and the absorption spectrum of the vapour have already been dealt with in Chapter III. (p. 144). The relation of the fluorescent emission to the absorption is made clear by reference to the accompanying diagram of the first four energy levels of the atom. When thallium vapour at moderate temperatures (200° to 500° C.) is illuminated with the full light of the thallium arc, all four lines indicated in the diagram are observed in the fluorescent emission. Two of these lines are resonance lines of the normal (2^2P_1) atom, the other two are resonance lines of the metastable (2^2P_2) atom. The emission of the latter lines is not, however, consequent upon their absorption, since in the first place thallium vapour within the temperature range indicated does not appreciably absorb either at 5350 or at 3529 Å, and in the second place, if all wavelengths other than 5350 or 3529 Å are filtered from the exciting beam,

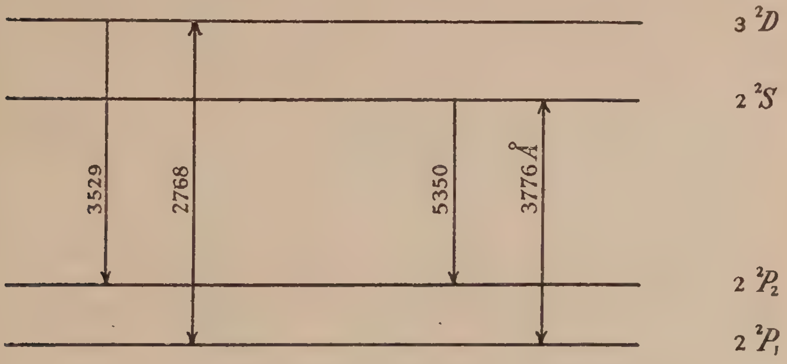

FIG. 35.—**Illustrating the fluorescence of thallium vapour.**

the fluorescence is completely extinguished. Terenin has in fact demonstrated that the emission of the green 5350 Å line is conditioned by absorption of the line at 3776 Å, and that a similar relationship exists between the emission of the 3529 Å line and absorption of the 2768 Å line. The explanation of these results is obvious from the diagram. When the normal thallium atom is raised by absorption to either the 2^2S or the 3^2D level it may either revert spontaneously to the normal state by emission of the absorbed line or it may pass spontaneously to the metastable (2^2P_2) state by emission of the 5350 Å or the 3529 Å line. Equally obvious is the explanation of the fact that when the temperature of the thallium vapour is raised to about 800° C. and an appreciable concentration of metastable atoms thereby maintained in the vapour, the thallium green line, which is completely ineffective at the lower temperatures, can now produce a fluorescent emission of both 5350 Å and 3776 Å. Results analogous to those obtained with thallium vapour have also been observed by Terenin in the fluorescent emission of lead, bismuth, and antimony vapours.

The thallium line 5350 Å which is absorbed and re-emitted in thallium vapour at temperatures of 800° C. and over is the true resonance line of the metastable atom. One or two other examples of resonance on the part of metastable atoms may be mentioned. In the section upon absorption by electrically excited atoms (p. 147) it was noted that, when a weak electric discharge is passed through helium at low pressure, the gas absorbs certain wave-lengths in the infra-red, visible, and near ultra-violet, where helium is normally transparent. This absorption is attributed to the maintenance, by the discharge, of appreciable numbers of parhelium (2^1S_0) atoms and particularly of metastable (2^3S_1) atoms. Absorption of the near infra-red doublet 10,829/30 Å, which takes the metastable (2^3S_1) atom to the $2^3P_{0,2}$ energy levels, is specially marked, and Paschen has observed that this doublet is also strongly emitted as fluorescence by the electrically excited and simultaneously illuminated gas. A similar absorption and fluorescent emission of the ultra-violet line 3889 Å, corresponding to the reciprocal transitions $2^3S_1 \rightleftharpoons 3^3P$, has been recorded by McCurdy. The attention of the reader may also be recalled to the fluorescence observed by de Grott (cf. p. 148) in electrically excited neon when illuminated with the visible radiation of a neon lamp. The corresponding fluorescence phenomena with electrically excited argon have been investigated by Meissner (*Z. Physik*, **43,** 449, 1927).

In the above cases of excitation in stages, the first stage of excitation is produced thermally or electrically, the second stage by illumination. Under suitable conditions, however, both stages of excitation may be photo-processes, in which case the resonance lines of *labile* as well as metastable states of the atom may be found in the fluorescent emission. The interesting fluorescence phenomena obtained under special conditions of illumination with mercury vapour have already been detailed in Chapter III.

We may conclude this section with a brief mention of the well-known generalisation proposed by Stokes which states that the frequency of the fluorescent emission should always be less than or at most equal to that of the exciting light. So far as it referred to strictly monochromatic illumination the law was of course very soon perceived to be honoured as much in the breach as in the observance, and the reason for its frequent failure is not far to seek. When restated in terms of the elementary quantum processes of absorption and emission, viz. the quantum of radiant energy emitted shall not exceed the quantum absorbed, we see at once that this condition is inevitable only provided (1) the absorbing unit starts from its lowest possible energy level, and (2) the unit has no opportunity of acquiring additional internal energy between the instants of absorption and emission. Various exceptions to Stokes' Law which may be traced to the non-fulfilment of the first proviso have been described above. Numerous examples of the non-validity of the law which can be referred to a breach of the second condition will be met with in the sequel.

RESONANCE SPECTRA OF DIATOMIC GASES AND VAPOURS.

Theoretical.—From what we know of the multiplicity of internal energy levels which the molecule, as compared with the atom, can assume, it is at once obvious that the photoluminescence spectra of polyatomic gases and vapours, even under the simplest experimental conditions, must always be much more complex than those of atoms. Before dealing with specific examples, it will be instructive to consider the type of fluorescence spectrum which we may expect from a gas or vapour composed of diatomic molecules. For simplicity, we will presume that the absorbing molecule is in the normal (i.e. the lowest electronic) state, and is brought by the act of absorption to a state of *electronic* excitation from which it can only revert spontaneously to the normal level. We will further presume that the pressure of the gas or vapour is low enough so that the possibility of any change in this state of excitation being induced by collisions during the life period of the activated molecule can be ignored. Finally, we will restrict ourselves at the outset to excitation by monochromatic illumination. These various conditions ensure that all frequencies in the emission spectrum will belong to the same *system* as the exciting frequency. The photoluminescence of a monatomic vapour under these same conditions would be a pure resonance—the emission of a single frequency identical with the exciting frequency. For the molecule, the corresponding emission spectrum is termed a "resonance spectrum."

Although limiting ourselves to absorption by molecules which are in the normal *electronic* state, there is no necessity to extend the restriction to absorption by molecules which are also at the zero level of vibrational and rotational energy (as a result of temperature equilibrium the absorbing system contains "normal" molecules with various possible vibrational and rotational energy contents). Suppose that the initial state of the molecules which are capable of absorbing the exciting frequency ν_a is defined by the quantum numbers (n', p', m') and that by absorption these molecules momentarily attain the state (n'', p'', m''). The exact reversal of this process of absorption would of course be $(n'', p'', m'') \rightarrow (n', p', m')$ with re-emission of the line ν_a, but there are other possibilities of spontaneous emission open to the excited molecule. In these no limitation is imposed on the change in the vibrational quantum number p'', but the rotational quantum number m'' can normally only increase or decrease by one unit. Distinguishing the vibrational and rotational quantum numbers of any state to which the excited molecule reverts by p and m respectively, the possible frequencies in the emission spectrum are given by

$$\nu = \frac{E_{n''} - E_{n'}}{h} + \frac{E_{p''} - E_p}{h} + \frac{E_{m''} - E_m}{h} \quad . \quad . \quad (1)$$

In applying this relation, p can have any integral value, and $m = m'' \pm 1$.

Equation (1) now requires to be evaluated for constant n', n'', p'', and m''. The variable term E_p/h is given by

$$E_p/h = (p + \tfrac{1}{2})\nu_v'\{1 - (p + \tfrac{1}{2})x'\} \quad . \quad . \quad . \quad (2)$$

(cf. equation (20*a*) of Chapter IV.), where ν_v' and x' refer to the normal state of the molecule. The other variable term E_m/h is given by

$$\begin{aligned} E_m/h &= B'm(m + 1) \\ &= B'(m + \tfrac{1}{2})^2 - \tfrac{1}{4}B' \\ &= B'(m'' \pm 1 + \tfrac{1}{2})^2 - \tfrac{1}{4}B' \quad . \quad . \quad (3) \end{aligned}$$

where the constant B' again refers to the normal state. Hence the frequencies of the resonance spectrum are fully expressed by the equation

$$\nu = \nu_0 - (p + \tfrac{1}{2})\nu_v'\{1 - (p + \tfrac{1}{2})x'\} - B'(m'' \pm 1 + \tfrac{1}{2})^2 \quad . \quad (4)$$

with p the only variable on the right-hand side and with

$$\nu_0 = \frac{E_{n''} - E_{n'}}{h} + (p'' + \tfrac{1}{2})\nu_v''\{1 - (p'' + \tfrac{1}{2})x''\} \\ + B''(m'' + \tfrac{1}{2})^2 - \tfrac{1}{4}(B'' - B').$$

Equation (4) can obviously be simplified to the form

$$\nu = a - b(p + \tfrac{1}{2}) + c(p + \tfrac{1}{2})^2 - B'(m'' \pm 1 + \tfrac{1}{2})^2 \quad . \quad (5)$$

or

$$\nu = a - \beta p + \gamma p^2 - B'(m'' \pm 1 + \tfrac{1}{2})^2 \quad . \quad . \quad . \quad (6)$$

with $p = 0, 1, 2, 3, \ldots$ in either case.

This resonance spectrum has primarily the structure of a Deslandres first progression. Each member of the progression is not, however, a complete band (since m'' is not a variable) but a doublet, the two components corresponding to the choice of sign in the last factor, which choice can in turn be traced back, of course, to the two possible changes in the rotational quantum number of the emitting molecule. One feature of the spectrum to which special attention must be drawn is that the doublet separation should be the same for every member of the progression. This doublet separation is given by

$$\begin{aligned} \Delta\nu &= B'\{(m'' + 1 + \tfrac{1}{2})^2 - (m'' - 1 + \tfrac{1}{2})^2\} \\ &= 4B'(m'' + \tfrac{1}{2}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

The exciting line itself should of course be represented in the resonance spectrum by one component—the " main line " as it is termed—of the doublet for which $p = p'$. Whether or not this true resonance line, coinciding in frequency with the exciting line, happens to be the component of greater or smaller frequency of the doublet to which it belongs is in practice a matter of importance, since the alternatives decide whether in the process of excitation the rotational quantum number of the molecule has been increased or decreased by one unit. (It should be noted that in actual practice there is usually no *a priori* knowledge of the p' and m' of the molecule which absorbs the frequency used to produce the fluorescence, and the identity of this molecule can only be inferred from a detailed analysis of the inter-relations of the absorption and fluorescence spectra of the gas or vapour.) The two alternatives of spontaneous emission which would leave the excited molecule in its original state of electronic and vibrational energy content are $(n'', p'', m'') \rightarrow (n', p', m'' + 1)$ and $(n'', p'', m'') \rightarrow (n', p', m'' - 1)$, and it is the latter transition which gives the component of greater frequency in the doublet. If now this component coincides in frequency with the exciting line, it follows that in the original process of excitation the rotational quantum number changed from $m'' - 1$ to m'', that is, it increased by one unit. If, on the other hand, the component of smaller frequency is the true resonance line, the excitation process must have involved the transition $m'' + 1 \rightarrow m''$, that is, the rotational quantum number decreased by one unit. This criterion affords some help towards fixing the absolute values of the rotational quantum numbers involved in the processes of absorption and re-emission. The magnitude of the doublet separation $\Delta\nu$ of equation (7) is, of course, even more important in the same connection.

If the value of p', the vibrational quantum number of the molecule which absorbs the exciting line, is known, then since $p = p'$ for that line in the resonance spectrum which coincides in frequency with the exciting line, the p's of all the other lines in the resonance spectrum can immediately be evaluated. If p' is not known, its value can still be inferred with some degree of certainty from certain characteristics of the resonance spectrum. Without fore-knowledge of the p's of its various lines, this spectrum is empirically described in the following way. The doublet which contains the exciting line itself is called the doublet of zero order and the other doublets of the spectrum are reckoned as of $+^{\text{ve}}$ or $-^{\text{ve}}$ order according to their positions on the long or short wave-length side of this zero order doublet. Denoting the order of any doublet by the variable integral p_1, and remembering that $p = p'$ for the doublet of zero order, it is easily seen that $p_1 = p - p'$. The doublet of zero order is that emitted in the spontaneous transition $(n'', p'') \rightarrow (n', p = p')$ and that of order p_1 is emitted in the transition $(n'', p'') \rightarrow (n', p = p' + p_1)$. It should be clearly understood that the doublet of zero order as above defined is not that for which the true vibrational quantum number p is zero, unless the original excitation happens to have occurred in the vibrationless molecule $(p' = 0)$. The difference between the enumeration of the doublets in terms of their order p_1 and their enumeration in terms of the true quantum number p of the level to which the molecule falls is made clear by the diagram of Fig. 36.

The doublets of negative order, that is, those lying on the short wave-length side of the exciting line, are of particular significance for the evaluation of p'. The lines of these doublets are, of course, "anti-Stokes lines" in the sense that their frequencies are greater than the exciting frequency. When such lines occur in the resonance spectrum of a gas or vapour, their presence indicates that the absorbing molecules cannot before excitation have been at the zero level of vibrational energy. It is theoretically possible, therefore, to deduce from the observed number of doublets of negative order in the resonance spectrum which vibrational sub-level of the normal state is involved in the process of excitation. For example, in the case illustrated in Fig. 36, there are two doublets of negative order in the emission spectrum, hence $p' = 2$. This method of fixing p' and therefore the p's of the various lines in the resonance spectrum is extremely simple and useful, but, of course, some care is necessary in its application, since in practice one or more of the theoretically possible doublets of negative order may be present in the spectrum only with vanishingly small intensity and yet, if overlooked, the result would be vitiated.

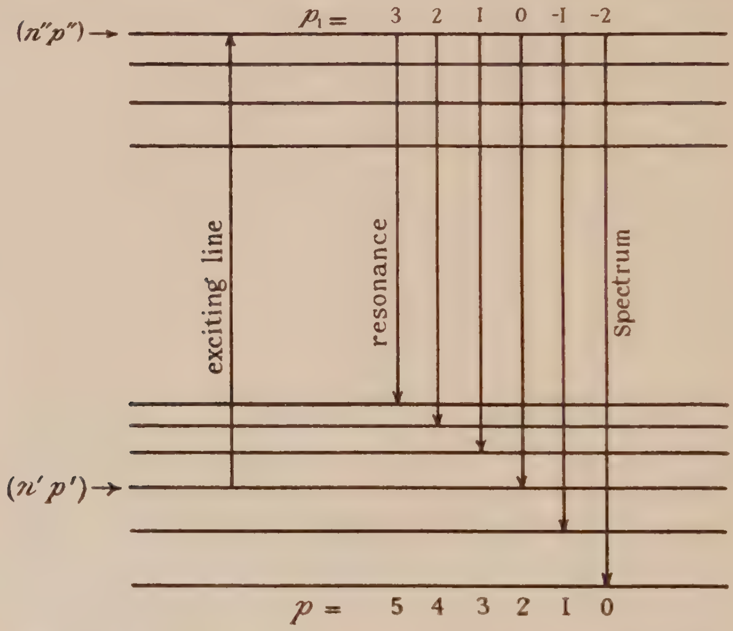

FIG. 36.—Resonance spectrum excited by monochromatic illumination.

If we change in equation (6) from the variable p to the variable p_1 by means of the relation $p = p_1 + p'$, and if we ignore the last term of (6) which merely takes account of the doublet structure, the series of frequencies in the resonance spectrum becomes

$$\nu = \alpha_1 - \beta_1 p_1 + \gamma_1 p_1^2 \qquad (p_1 = 0, \pm 1, \pm 2, \ldots).$$

Also when $p_1 = 0$, $\nu = \nu_a$, the frequency of the exciting line, so that we may re-write this as

$$\nu = \nu_a - \beta_1 p_1 + \gamma_1 p_1^2 \qquad \ldots \ldots (8)$$

In this equation β_1 and γ_1 are constants as are β and γ of equation (6), but they will in general differ in value from β and γ.

Equation (8) is indeed the type of empirical relation which is found in practice to hold between the positions of the lines in a resonance series, their order numbers p_1, and the frequency ν_a of the exciting line, and from this we can obviously reverse the deduction of (8) from (6) or (5) and so justify these theoretical forms of the progression law. It should be noted that it is always necessary to work back from (8) to (5) or (6) in order to evaluate the vibrational constants ν_v' and x' of the molecule in its normal state from the empirical constants β_1 and γ_1 of the resonance series, and to do this a knowledge of p' is, of course, essential.

So far, we have only considered the fluorescent emission to be expected from a diatomic gas or vapour at low pressures when illuminated with strictly monochromatic light, it being thereby implied that the exciting line is so narrow as to cover one and only one fine line of the absorption spectrum of the gas. Since, however, the individual lines of an absorption spectrum are sometimes very much crowded together in certain spectral regions, it may happen that a comparatively narrow exciting line will cover more than one absorption line. In this event, more than one type of excited molecule may be formed, and the resonance spectrum obtained will be correspondingly more complex. From the various possibilities we need only select one or two particular examples.

(*a*) The exciting line covers two lines belonging to the same absorption band of the gas or vapour. If these lines happen to correspond to the rotational transitions in absorption $(m'' - 1) \rightarrow m''$ and $(m'' + 1) \rightarrow m''$, then only one type of excited molecule is formed, namely that represented by (n'', p'', m''), and the resonance spectrum consists of a single progression of doublets as above described. In general, however, we may expect two types of excited molecule, differing in their state of rotation, which we may represent by (n'', p'', m_1'') and (n'', p'', m_2''). The fluorescent emission will then consist of two progressions of doublets, both of the type (6), with identical values of their β's and γ's, and differing only slightly in respect of the absolute values of α, but with different values of m'', and therefore different doublet separations. The doublet separation in the one progression will be $\Delta_1\nu = 4B'(m_1'' + \frac{1}{2})$, that in the other progression will be $\Delta_2\nu = 4B'(m_2'' + \frac{1}{2})$.

(*b*) The exciting line is wide enough to include lines belonging to two consecutive absorption bands. This may happen for a comparatively narrow exciting line if the absorption bands overlap. If only one fine line of each band were covered by the exciting line, we should obtain two progressions of doublets of type (6) in the fluorescence. These progressions would normally differ not only in respect of their doublet separations, but also in other particulars. We have to distinguish three cases. (1) When the adjacent absorption bands in question refer to different vibrational levels of the normal molecule but the same vibrational level of the excited molecule, the two sets of doublets in the emission belong to the same Deslandres first progression (α, β, and γ the same), and the spectral positions of corresponding doublets differ only in so far as the m'''s of the excited states differ. One series will have one doublet of negative order more than the other. (2) If the adjacent absorption bands refer to the same vibrational level of the normal molecule but different vibrational levels of the excited molecule, the two sets of doublets in the emission belong to different Deslandres first progressions (β and γ the same, α different), but they have the same number of doublets of negative order. (3) When both the initial and final states are different in the two excitation processes, the two sets of doublets in the resonance spectrum will belong to different Deslandres first progressions, and will also have different numbers of doublets of negative order. These conclusions may be more readily grasped by extending the diagram of Fig. 36 to take account of the different possibilities considered.

Finally, we may ask what sort of fluorescence spectrum is to be expected when a diatomic gas is illuminated with a continuous spectrum extending over the whole range of its band absorption. In this case we must note that at moderate temperatures we have present in the gas normal molecules with a very large range of values of m'. The continuous spectral region covering the single absorption band $(n', p') \rightarrow (n'', p'')$ will therefore produce excited molecules with a correspondingly wide range of values of m'', and these molecules by spontaneous emission will now give a progression not of doublets but of filled-up bands. Each member of the progression will, in fact, be filled up with fine lines to practically the same extent as the absorption band from which it derives. The complete fluorescence spectrum may, however, contain many more bands than the absorption spectrum itself does under the same conditions. The temperature of the gas limits the vibrational quantum number p' of the lower state in absorption to a few values, but no such limitation is imposed upon the vibrational quantum number p of the lower state in the subsequent emission process. Hence, while the absorption spectrum of a gas at moderate temperatures can contain only a few progressions of bands, the fluorescent emission caused by this absorption may contain numerous other progressions not present in the absorption spectrum. The fluorescence spectrum produced by continuous illumination thus approaches more nearly to the " complete " emission spectrum of the gas which would result from its excitation by an electrical discharge.

Resonance Spectra of Iodine Vapour.—The fluorescence of iodine vapour under different conditions of excitation provides the best investigated practical illustrations of the theory of resonance spectra. Iodine vapour at ordinary temperatures absorbs discontinuously in the visible from about 700 to 500 $\mu\mu$, the absorption spectrum within these limits consisting of thousands of fine lines which are grouped into a large number of bands of normal type. The classification of these bands into progressions, corresponding to absorption by molecules in different vibrational sub-levels of the normal state, has already been discussed in another connection. In some places the individual absorption lines are very much crowded together due to overlapping of the bands of different progressions. This happens, for example, in the region of the mercury green line at 5462 Å, with consequences in fluorescence which will be described below.

When iodine vapour at low saturation pressures and in the absence of foreign gases is excited by white light, as for example when an evacuated glass bulb containing a few crystals of solid iodine is illuminated with sunlight at room temperature, a bright yellow-green fluorescence results. This fluorescence when spectrally resolved is found to have much the same complex band structure as the absorption spectrum itself. A very great simplification in the fluorescent emission is, however, brought about by illuminating the vapour with strictly monochromatic light of a wave-length lying in the absorption region. Of the various resonance spectra resulting from such illumination which have been recorded, we may deal particularly with that which is excited by the mercury line at 5462 Å. This resonance spectrum has been specially investigated by R. W. Wood (*Phil. Mag.*, [vi.], **35,** 236, 252, 1918) to whom, indeed, the bulk of our experimental data on the absorption and fluorescence of iodine vapour is due. The first point to note is that the green line at 5462 Å, as ordinarily obtained from a quartz mercury vapour lamp run hot under a fairly heavy current, is not sufficiently monochromatic to excite a single resonance series in iodine. This line may in fact be over half an Ångström unit in width and broad enough to cover many individual absorption lines of iodine vapour. The green line can, however, be narrowed sufficiently to cover only one absorption line if the lamp is run cold and under a low current density. When iodine vapour is illuminated with the sharp line so obtained, a pure resonance spectrum results. This consists of a long series of doublets stretching from the green to the red with a practically constant doublet separation of 5 cm.$^{-1}$ and an approximately constant spacing of the consecutive doublets of 200 cm.$^{-1}$ More accurately, however, the series converges slowly towards the red in the manner of a Deslandres first progression. The doublets actually obtained by Wood are given in wave-lengths and also in wave-numbers in Table XXVI. Further members of the series in the red and near infra-red up to 8823 Å ($p_1 = 37$) have been reported more recently by Oldenberg (*Z. Physik*, **45,** 451, 1927).

The exciting line itself is represented in this resonance spectrum by the line of shortest wave-length, and since the doublet to which this belongs is the doublet of zero order ($p_1 = 0$), all the other doublets are of positive order, as indicated in the table. Expressing the wave-numbers in terms of a series of powers of p_1, Loomis (*Bull. Nat. Research Council*, **11,** Pt. 3, 272, 1926) finds that the " main " lines of the series (the shorter wave-length components of the doublets in the present instance) are very accurately represented by the progression law

$$\nu = 18307{\cdot}5 - 213{\cdot}67p_1 + 0{\cdot}592p_1^2 + 0{\cdot}0021p_1^3 \quad . \quad (9)$$

which, apart from the small term in p_1^3, is of the same form as (8) above. From the fact that there are no doublets of negative order in the resonance spectrum, it follows that the molecule which absorbs and re-emits the zero-order line 5462 Å starts from and reverts to the lowest possible vibrational sub-level of the normal state, viz. $p' = 0$.

TABLE XXVI.

RESONANCE SPECTRUM OF I_2 VAPOUR EXCITED BY NARROW Hg LINE 5462 Å.

Order of Doublet.	Wave-length λ(Å).	Wave-number ν(cm.⁻¹).	Order of Doublet.	Wave length λ(Å).	Wave-number ν(cm.⁻¹).
0	5462·23	18307·5	14	missing	—
	5463·74	18302·5	15	6560·56	15242·6
1	5526·55	18094·5		6562·68	15237·7
	5528·10	18089·4	16	6645·0	15048·9
2	missing	—		6647·0	15044·3
3	5658·71	17671·9	17	6731·12	14856·4
	5660·38	17666·7		6733·28	14851·6
4	5726·59	17462·4	18	6618·63	14665·7
	5728·25	17457·3		6820·01	14660·8
5	5795·79	17253·9	19	faint	—
	5797·51	17248·8	20	6908·96	14287·8
6	5866·14	17046·9		7001·39	14282·8
	5867·85	17042·0	21	missing	—
7	missing	—	22	7186·23	13915·5
8	6010·66	16637·1		7188·68	13910·7
	6012·50	16632·0	23	7282·39	13731·8
9	missing	—		7284·92	13727·0
10	6160·63	16232·1	24	missing	—
	6162·48	16227·2	25	7480·4	13368·2
11	6237·68	16031·6		7482·9	13363·8
	6239·56	16026·8	26	missing	—
12	6216·16	15832·4	27	7685·7	13011·0
	6218·14	15827·0		7688·5	13006·0
13	6396·08	15634·6			
	6398·05	15629·7			

The order number of any other doublet therefore gives directly the vibrational sub-level of the normal state to which the excited molecule reverts in emitting it, and equation (9) holds with exactly the same coefficients when p is substituted in place of p_1. We thus have excited molecules passing spontaneously from the excited state (n'', p'', m'') to all * vibrational sub-levels of the normal state from $p = 0$ to $p = 37$,

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* The practical absence of the members $p_1 = 2, 7, 14, 21, 24$, and 26 in the resonance series observed by Wood means that the particular transitions involved in them are intrinsically very improbable compared with the others. It should be remarked that among these others the intensity varies in an irregular manner. The relation of intensity to the quantum transition involved cannot, however, be adequately dealt with here (cf. p. 214).

and equation (9) affords a direct means of evaluating the successive vibration quanta of the normal iodine molecule. One further point can be inferred directly from the resonance spectrum itself, namely, that since the pure resonance line 5462 Å is the shorter wave-length component of the doublet to which it belongs, the rotational quantum number of the molecule must have been *increased* by one unit in the process of absorption, that is, the absorption line of iodine covered by the sharp 5462 Å mercury line is a member of the R branch of the band to which it belongs. The actual values of the vibrational and rotational quantum numbers p'' and m'' of the excited state from which all the resonance doublets derive cannot, however, be inferred from the resonance spectrum alone. To obtain these a very tedious analysis and correlation of the resonance and absorption spectra of iodine vapour are necessary. Without entering into the details, for which the reader may be referred to the article of Loomis mentioned above, it transpires that the upper state of excitation of the iodine molecule concerned in the emission of this resonance series is such that $p'' = 26$ and $m'' = 34$, and the absorption line of iodine which produces this state of excitation is the line (0, 33) → (26, 34).

TABLE XXVII.

Resonance Series of I_2 Vapour Excited by Broad Hg Line 5462 Å.

Absorption Line Concerned.		Doublet Separation $\Delta\nu$ (cm.$^{-1}$).
$p' \to p''$.	$m' \to m''$.	
0 → 26	29 → 28	+ 4·3
	30 → 29	+ 4·4
	33 → 34	− 5·0*
	34 → 35	− 5·2
0 → 27	81 → 80	+ 12·0
	84 → 85	− 12·73
0 → 28	109 → 108	+ 16·13
0 → 29	130 → 129	+ 19·26
	133 → 134	− 19·9
1 → 29	46 → 45	+ 7·2
	49 → 50	− 6·6
	50 → 51	− 8·3

When iodine vapour is illuminated with the broad green " line " of a hot mercury arc, which as already noted covers several of its individual absorption lines, several different upper states of excitation of the molecule are made possible, and a corresponding number of different resonance series of doublets appears in the fluorescent emission. Each of these series contains a true resonance line, that is, a line covered by some part of the broad exciting mercury line, and the spacings of consecutive doublets is either identical or nearly so in the different series, so that the general appearance of the fluorescence spectrum is that of a single resonance series with several components to each "doublet" instead of only two. An analysis of the spectrum into its individual resonance series and a careful study of the relation of these to each other has been carried out by various workers. Table XXVII. summarises the characteristics of the different series in respect of their doublet separations and of the vibrational and rotational quantum numbers of the absorption lines concerned in their excitation. A positive doublet separation means that the companion of the pure resonance line in the doublet of zero order lies on its short wave-length side, and this corresponds to a decrease of the rotational quantum number in the primary process of absorption. The reverse is implied by a negative doublet separation. The series distinguished by an asterisk is that which has been discussed in detail above.

All but the last three of the above resonance series are without terms of negative order (anti-Stokes terms) and therefore derive from absorption by the vibrationless molecule. The series group themselves according to the absorption band from which they derive, and it will be noted that, while the m'''s concerned are all of the same order of magnitude for the different series of any one group, there is a large alteration in m'' in passing from one group to another. This is clearly necessary if absorption lines corresponding to different inputs of vibrational energy are nevertheless to occupy the same narrow spectral region—the width of the exciting mercury line. Otherwise expressed, when two bands such as $(0 \rightarrow 26)$ and $(0 \rightarrow 29)$ belonging to the same progression overlap one another, the region of overlapping must correspond to very different parts of the two bands. The tail (for which m'' is large) of the $(0 \rightarrow 29)$ band overlaps the head (for which m'' is small) of the $(0 \rightarrow 26)$ band. Corresponding to the large range of values of m'', the values of the doublet separations $\Delta\nu$ also cover a large range and in the sense predicted by equation (7), that is, $\Delta\nu$ increases more or less proportionately to m''.

Each of the last three resonance series possesses one doublet of negative order, so that these series derive from absorption by iodine molecules already endowed with one quantum of vibrational energy. Molecules with more than one vibrational quantum are few in number in iodine vapour at ordinary temperatures—each vibrational quantum is equivalent to 213 cm.^{-1} or about 600 calories—so that resonance series with more than one doublet of negative order should appear, if at all, with relatively feeble intensity. Actually a faint series with two doublets of negative order is also observed in the fluorescence excited by the broad green line at ordinary temperatures. When, however, the vapour is heated at constant pressure, this series brightens in intensity compared with the others, and at 300° C. Pringsheim (*Z. Physik*, **7**, 206, 1921) has noted the presence in the fluorescence spectrum of resonance series with four and five doublets of negative order, series which must refer back to absorption by iodine molecules already possessing four and five vibration quanta. The proportion of such molecules present in the vapour would naturally increase rapidly with increasing temperature.

The capacity to excite iodine vapour to fluorescence is not of course confined to the very limited spectral region covered by the mercury green line. Theoretically any wave-length in the whole range of the visible band absorption which the vapour can absorb should be capable of exciting resonance series of the same type as described above, and Dymond (*Z. Physik*, **34,** 553, 1925) has in fact recorded a number of such series excited by various emission lines of Hg, Zn, Cd, Cu, and Na, the wave-lengths of which cover the spectral range from 500 to 600 $\mu\mu$. These resonance spectra possess no special features which would justify further discussion here, but one other observation of Dymond in relation to iodine fluorescence may be recalled. Dymond finds that, while all exciting frequencies lying within the compass of the visible band absorption of iodine vapour produce fluorescence, frequencies belonging to the region of continuous absorption of the vapour which begins at 500 $\mu\mu$ are totally ineffective. This, it may be remembered, is an important piece of evidence in favour of the concept of complete dissociation of the molecule into atoms by absorption in the continuum.

Besides the absorption band system in the visible, iodine vapour exhibits another region of discontinuous band absorption in the far ultra-violet beyond 200 $\mu\mu$, and illumination of the vapour with light of this region is likewise capable of exciting a fluorescent emission. The fluorescence obtained with monochromatic ultra-violet illumination was studied first by McLennan (*Proc. Roy. Soc.*, **88**A, 289, 1913; **91**A, 23, 1914) and later by Oldenberg (*Z. Physik*, **18,** 1, 1923; **25,** 136, 1924). For purposes of description the emission spectrum may be divided into two parts. The one part of the fluorescence, which extends over the same region as the ultra-violet band absorption, is a resonance series of doublets of essentially the same type as the visible resonance series—in fact, the various ultra-violet resonance series which can be excited by various lines differ from one another and from the visible resonance series of Wood and Dymond only in so far as they require different values of α in the series formulation (6); the β's and γ's have all the same numerical values. Thus, the zinc line 1900 Å excites an ultra-violet resonance series stretching from about 220 to 186 $\mu\mu$ and consisting of 35 positive and 5 negative doublets, which series is represented equally as well as the series of Table XXVI. by Loomis' empirical equation (9), only with the 18307·5 term replaced by 52604 cm.$^{-1}$, the wave-number of the pure resonance line 1900 Å. This clearly means that the ultra-violet and the visible resonance spectra involve the same *lower* electronic level of the molecule, namely the normal level. They differ, as do also the band absorption systems which produce them, in regard to the upper state of electronic excitation involved. Besides these resonance series, however, the fluorescent emission of iodine when excited by wavelengths below 200 $\mu\mu$ contains also a complex system of diffuse *bands* which stretch from 200 $\mu\mu$ into the visible. Unlike resonance series, the positions and relative intensities of these bands are independent of the exciting wave-length. Moreover, their structure and spacing show that the energy levels of the molecule directly involved in their emission bear no relation to any of the three main energy levels concerned in the visible and ultra-violet absorption and resonance. In particular, the normal energy level of the iodine molecule is not involved, since this band spectrum has never been obtained in absorption. A very similar emission spectrum is, however, obtained by electrical excitation of iodine vapour. The most probable explanation of the ultra-violet band fluorescence spectrum of iodine is that it represents one stage in a step-wise return to the normal of the molecule excited by ultra-violet absorption.

Fluorescence of Other Diatomic Gases and Vapours.— Fluorescence and resonance spectra have been obtained, especially within recent years, in several cases other than that of iodine vapour, and when observed such spectra have often played a useful rôle in the analysis of the absorption and emission band systems to which they belong. It may not perhaps be amiss to emphasise that a resonance series, excited by monochromatic illumination, gives directly the spacings and the correct assignment of quantum numbers of the vibrational sub-levels of the molecule in the lower of the two electronic states concerned in its emission ; the value of such information in the laborious analysis of the complete band system to which the resonance series belongs may easily be appreciated. It may also be mentioned that the fluorescent emission of certain metal vapours under suitable conditions of illumination bears out the fact, also suggested by their absorption spectra, that these vapours, which for all other purposes are taken as monatomic, may nevertheless contain minute but optically appreciable proportions of diatomic molecules. Before considering the fluorescence of these metal vapours, however, we will briefly review the existing data for other diatomic gases and vapours, elementary and compound, the absorption spectra of which have been referred to in the preceding Chapter.

Bromine and Chlorine.—Wood (*Phil. Mag.*, **21,** 309, 1911) and also Daure (*Compt. rend.*, **183,** 31, 1926) have reported a feeble green fluorescence in bromine vapour excited by direct sunlight at pressures below 1 mm. Hg. The most effective exciting wave-lengths appear to lie between 560 and 500 $\mu\mu$, a region which, it may be noted, covers the position of the absorption bands of the normal vibrationless molecule. At higher pressures the fluorescence disappears completely, and even at its maximum intensity the emission is much too weak to permit of its detailed investigation. Chlorine, when illuminated with radiation corresponding to its region of band absorption, gives no measurable fluorescent emission whatever the pressure. This complete absence of fluorescence in chlorine must be ascribed to the fact that fairly high pressures of the gas are required for appreciable absorption (its absorption coefficient is very much less than that of iodine vapour), and at such pressures the possibility of spontaneous re-emission by the excited molecules is prevented by collisions or even by the proximity of other chlorine molecules. This " damping " effect of pressure, which is a common feature in photoluminescent phenomena, is shown in the case of iodine vapour by the fact that, with a constant intensity of illumination, the intensity of fluorescence, which increases proportionately with pressure at low pressures, reaches a maximum at $p_{I_2} = 0{\cdot}3$ mm. Hg, and thereafter falls off very rapidly to zero. The efficacy of pressure damping of a gas seems to be a function of its electronegative character, and it is probably even more marked for bromine and chlorine than for iodine.

Sulphur, Selenium, and Tellurium.—The vapours of these elements, which are of distinctly less electronegative type than the halogens, possess marked powers of fluorescence when illuminated at temperatures between 400° and 800° C. with light which falls within their band absorption systems. The limits of the band absorption and corresponding fluorescence spectra are as follows :—

	Band Absorption.	Fluorescence.
Sulphur . .	4000-2548 Å	5650-2800 Å
Selenium .	4180-3238	4910-3500
Tellurium .	6200-3831	6600-4200

Fluorescence is in each case first noticeable at pressures of the order of 10^{-3} mm. Hg, and its intensity increases markedly with increasing pressure up to about 1 mm. Beyond this, volume fluorescence gradually passes over into surface fluorescence, but the latter persists up to much higher pressures than in the case of the halogens—250 mm. for sulphur, 50 mm. for selenium, and 30 mm. for tellurium vapour. For monochromatic illumination of any of the vapours within the limits of its band absorption, Rosen (*Z. Physik*, **43,** 69, 1927) has obtained resonance series of essentially the same type as those of iodine. In certain of these resonance series the doublet nature of the individual members is clearly shown. The seat of emission is identified by Rosen with the diatomic molecule of sulphur, selenium, or tellurium, which is also the unit concerned in the band absorption, and Rosen's detailed analysis and correlation of the fluorescence and absorption spectra show that the same two combining states of the molecule are concerned in the two reciprocal processes. Certain results of McLennan and Walerstein (*Physical Rev.*, **29,** 208, 1927) indicate that for selenium vapour at lower temperatures a fluorescence spectrum different from that of Rosen and stretching from the visible to 220 $\mu\mu$ can be excited by the short wave light of a quartz mercury arc. It is possible that, like iodine, the diatomic molecule of selenium may have two different band absorption systems and two corresponding regions of fluorescence, but it is also possible that McLennan's fluorescence spectrum which is excited at lower temperatures may belong to a more complex selenium molecule.

Nitrogen, Oxygen, and Hydrogen.—The absorption band systems of these gases lie in the extreme ultra-violet, and thus excitation to fluorescence should require correspondingly short wave-length radiation. Meyer and Wood (*Phil. Mag.*, **30,** 449, 1915), by illuminating air with light of wave-length below 150 $\mu\mu$, have obtained a fluorescent emission containing several bands belonging to the second positive group of nitrogen, and Oldenberg (*Z. Physik*, **38,** 370, 1926) has observed a fluorescence in nitrogen, excited at low pressures by similar short wave-length radiation, which comprises bands characterising both the neutral N_2 and the ionised N_2^+ molecule. This fluorescence spectrum stretches from the blue into the near ultra-violet. Oldenberg has likewise obtained a strong visible fluorescence from oxygen which is illuminated at low pressure with radiation below 130 $\mu\mu$. The elementary processes concerned in either case are not yet properly understood. From the great disparity in the positions of the exciting and fluorescence wave-length limits, however, it would appear certain that the phenomena are not of the nature of simple resonance. When hydrogen at low pressures is illuminated with very short wave-length light, no trace of the " many lines spectrum " which characterises the molecule is obtained, but the fluorescent emission contains the first few lines of the Balmer series of the hydrogen atom. Oldenberg considers that under the conditions of experiment the possibility of secondary dissociation (by collision) of an excited hydrogen molecule must be excluded, and that the atom lines must therefore derive from a primary photo-dissociation of the hydrogen molecule into a normal and an excited atom. The fluorescence is, according to this view, of essentially the same type as the D line emission observed by Terenin (cf. p. 227) when the vapour of sodium iodide is illuminated with ultra-violet light of $\lambda < 2450$ Å.

Heteropolar Molecules.—The vapours of the hydrogen halides and the alkali metal halides possess no band absorption but only regions of continuous absorption which point to the primary dissociation of the absorbing units. No band fluorescence is therefore expected to result from their illumination. The atom line fluorescence which is instead obtained in certain cases has already been discussed in the preceding Chapter. The silver halide vapours exhibit strong band absorption followed by continuous absorption in the near ultra-violet, and when any one of these vapours is excited at low pressures with monochromatic light of wave-length within the limits of its band absorption, resonance series are obtained of the same type as those of iodine, sulphur, selenium, etc. From the characteristics of these resonance series, Franck and Kuhn (*Z. Physik*, **43,** 164, 1927 ; **44,** 607, 1927) have deduced the strengths of binding of the normal silver halide molecules, and have formed from the optical data rough estimates of their heats of dissociation which support the view that the nuclear binding in these molecules is of the atomic and not of the ionic type. Finally, we may mention the fluorescence excited in the mercury halide vapours at low pressures by illumination with light of wave-length below 220 $\mu\mu$. Terenin (*Z. Physik*, **44,** 713, 1927) finds that each mercuric halide vapour emits under these conditions a strong visible fluorescence—green for $HgCl_2$, blue for $HgBr_2$, violet for HgI_2—which decomposes spectrally in each case into a complex system of bands running from the visible into the near ultra-violet. This fluorescence cannot be regarded as a resonance emission by excited HgX_2 molecules, since on the one hand the mercury halide vapours do not themselves absorb in the region of fluorescence, and on the other hand there is no fluorescent emission in the far ultra-violet region (220 — 180 $\mu\mu$) within which the vapours do absorb. For these and other reasons, Terenin has been led to conclude that the fluorescence derives, not from an excited HgX_2 molecule, but from an activated diatomic molecule HgX^* which is one of the products of a primary dissociation process: $HgX_2 \rightarrow HgX^* + X$, caused by the light absorption. The energy necessary for the dissociation of HgX_2 into normal (non-activated) Hg X and X is about 50 kilo-calories, while the quantum of radiant energy actually supplied to the HgX_2 molecule is about 140 kilo-calories, so that it is quite possible for the one product HgX^* of the optical dissociation to have sufficient excess energy to give a visible and near ultra-violet fluorescence.

The Alkali Metals.—A very extensive series of investigations has been carried out within the last twenty years by Wood and co-workers upon the band absorption and fluorescence of sodium vapour. This vapour, when illuminated at the saturation pressure corresponding to 300° C. or over with white light, gives a strong *green* fluorescent emission which contains, besides the yellow resonance doublet characteristic of the sodium atom itself, two systems of channelled bands, the one in the blue-green (460-550 $\mu\mu$), the other in the orange-red (600-700 $\mu\mu$). Under similar conditions of illumination, the vapour exhibits band absorption in the same two regions. In the earlier stages of investigation, some difficulty was experienced in deciding whether these band systems were to be ascribed to sodium molecules or to sodium compounds or simply to traces of impurities present in the vapour. Without entering into details, it now appears reasonably certain (cf. Pringsheim, *Z. Physik*, **38,** 161, 1926) that the band systems in the blue-green and orange-red are indeed characteristic of a diatomic Na_2 molecule. Other band systems may, however, be obtained both in the fluorescence and in the absorption of impure sodium vapour—for example, the intense orange-yellow band system mentioned below which is present in the absorption and fluorescence of sodium vapour contaminated with potassium, and which is supposed to derive from a K—Na complex.

The fluorescence of sodium vapour is very much simplified when the vapour is excited, not with full white light, but with individual wave-lengths which it can absorb either in the green or in the red.

The emission then consists of a simple resonance series of lines or doublets, which contains the exciting line itself as one member, and which lies entirely in the blue-green or in the orange-red according to the absorption range within which the exciting wave-length falls. A great number of such resonance series excited by different monochromatic radiations have been investigated by Wood and co-workers. For purposes of illustration we may tabulate two of Wood's series, one in the blue-green, the other in the red, which are excited in sodium vapour at about 500° C. by the magnesium line 5173 Å and the lithium line 6102 Å respectively.

TABLE XXVIII.

Resonance Series of Na Vapour Excited by the Lines 5173 Å and 6102 Å.

Order Number p_1.	λ(Å).	ν cm.$^{-1}$).	$\Delta\nu$.	Order Number p_1.	λ(Å).	ν(cm.$^{-1}$).	$\Delta\nu$.
− 6	4946	20219	155	− 3	5942	16825	157
− 5	4984	20064	152	− 2	5998	16668	135
− 4	5022	19912	149	− 1	6047	16533	152
− 3	5060	19763	148	0	*6102*	16381	146
− 2	5098	19615	145	1	6158	16235	157
− 1	5136	19470	141	2	6218	16078	151
0	*5173*	19329	142	3	6277	15927	154
1	5212	19187	139	4	6338	15773	143
2	5250	19048	137	5	6396	15630	
3	5288	18911	138				
4	5327	18773					

The series in the green is clearly of the nature of a first progression, that is to say, its different lines connote transitions of the primarily excited molecule to different vibrational sub-levels of a lower electronic state. The progression law is not so apparent in the red series, but there can be little question that its individual lines must be similarly interpreted. One important point to note is that the spacing of the lines is the same in both series, and, moreover, essentially the same line spacing is obtained in all the other resonance series of sodium vapour in the red and in the green. All the resonance series are in fact represented (when true vibrational quantum numbers are used in place of order numbers) by the one progression law

$$\nu = \alpha - 158{\cdot}5p + 0{\cdot}73p^2,$$

wherein only the value of the series constant α differs from one series to another. This result must mean (*a*) that both the red and the green absorption and fluorescence bands derive from the same molecule, (*b*) that the same *lower* electronic state of this molecule is concerned for both spectral regions. Following from this, it is naturally assumed that it is the *normal* Na_2 molecule which absorbs both in the red and in the green, and that the fluorescent emission results in both instances from the return of excited molecules to the normal state. It must not be inferred, however, that the Na_2 molecule attains the same state of electronic excitation by absorption in the red as in the green. On the contrary, the red and the green absorption and fluorescence bands appear to belong to quite independent systems and therefore to involve two distinct states of excitation of the molecule. They are, in fact, analogous to the two independent systems of bands which iodine vapour exhibits in the visible and ultra-violet.

With the help of the information regarding the vibrational sub-levels of the normal Na_2 molecule which is afforded by the resonance series, Loomis (*Physical Rev.*, **29,** 607, 1927) has effected an unambiguous assignment of vibrational quantum numbers p' and p'' to the absorption and fluorescence bands of sodium vapour in the blue-green. The complete band system is represented by

$$\nu = 20301{\cdot}7 + (124{\cdot}13p'' - 0{\cdot}84p''^2) - (158{\cdot}5p' - 0{\cdot}73p'^2),$$

from which it is seen that the first vibration quanta of the molecule in the normal and excited states are, in round numbers, 158 and 124 cm.$^{-1}$ respectively. That $\Delta''\nu$ should be less than $\Delta'\nu$ is in agreement with the fact that the absorption and fluorescence bands all degrade towards the red ($I'' > I'$). Again, by extrapolation of the vibrational sub-levels of the normal and of the excited molecule to zero separation, Loomis (*ibid.*, **31,** 323, 1928) has estimated the heat of dissociation of the *normal* Na_2 molecule into two normal atoms as $1{\cdot}0 \pm 0{\cdot}1$ volts (23 kilo-calories), and that of the *excited* Na_2 molecule, presumably into an excited Na* and a normal Na atom, as 0·57 volt (13 kilo-calories). Taking into account the fact that the vibrationless excited molecule has already an excess energy content equivalent to 20301·7 cm.$^{-1}$ or 2·50 volts, it follows that the products of optical dissociation of the excited Na_2 molecule (by absorption at a hypothetical convergence limit to the above blue-green band system) have an amount of energy above that of two normal sodium atoms equal to $2{\cdot}50 + 0{\cdot}57 - 1{\cdot}0 = 2{\cdot}07$ volts. The excess energy of a 2^2P sodium atom, however, is 2·10 volts, so that the optical dissociation envisaged is clearly

$$Na_2 + h\nu_c \rightarrow Na(1^2S) + Na(2^2P).$$

What the corresponding dissociation process at the convergence limit of the orange-red band system would be, remains uncertain.

By exciting sodium vapour with ultra-violet light, Wood has obtained another region of fluorescence lying in the neighbourhood of the 3302/3 Å emission doublet of the atom. This fluorescence is probably the counterpart of the absorption band system of the vapour which lies in the same spectral region (cf. p. 143), but it has not yet been examined in any detail. It is probable that there are other regions of ultra-violet fluorescence of the vapour corresponding to the band absorption which accompanies each of the higher members of the atom's Principal Series.

Just as in sodium vapour the D lines are flanked by two independent regions of band absorption, so also in potassium vapour at moderate temperatures (250° C. upwards) there are two systems of absorption bands lying to right and left of the principal doublet 7699/65 Å of the atom in the red. Fluorescence and resonance emission of potassium vapour on the short wave-length side of this doublet have been observed by Wood and Carter (*Physical Rev.*, **27**, 107, 1908) and also by Pringsheim and Rosen (*Z. Physik*, **43**, 519, 1927). By excitation of the vapour with the monochromatic zinc line 6362 Å, a simple resonance series of almost equally spaced lines is obtained. Excitation with white light gives a whole system of fluorescence bands between 600 and 700 $\mu\mu$ which Pringsheim and Rosen have arranged into p' and p'' progressions. The complete band system is approximately represented (with the omission of squared terms) by

$$\nu = 16{,}103 + 74p'' - 90p',$$

from which it follows that the first vibration quanta of the normal and excited K_2 molecules are about 90 and 74 cm.$^{-1}$ respectively. The first vibration quantum of the normal K_2 molecule is much less than that of the normal Na_2 molecule, indicating a much looser binding in the former case, and therefore we should expect the heats of dissociation of the two molecules to be decidedly different. In agreement with this, the heat of dissociation of Na_2 is about 23 kilo-calories, while that of K_2, indirectly estimated by Pringsheim and Carrelli (*Z. Physik*, **44**, 643, 1927) from the variation with temperature and pressure of the brightness of the red fluorescence of potassium vapour, is about 14 kilo-calories. A slightly higher estimate, viz. 16 kilo-calories, is obtained by extrapolation of the vibrational sub-levels of the normal molecule to zero separation.

The heats of dissociation of these alkali metal molecules may at first sight appear surprisingly high in view of the fact that ordinary methods fail to reveal the existence of diatomic molecules in the vapours under any conditions of temperature or pressure. Actually, however, Pringsheim and Carrelli's value for the heat of dissociation of the K_2 molecule means that only 3 in every 1000 atoms exist in the combined state in the saturated vapour at 277° C. Since the saturated vapour pressure of potassium at this temperature is only about one-tenth of a millimetre, it follows that the quite appreciable band absorption and fluorescence of potassium vapour at 277° C. derive from diatomic molecules at a partial pressure of about 3.10^{-4} mm. The association of atoms to form molecules is, of course, favoured by high pressures, but high pressures of potassium vapour can only be obtained by increasing the temperature which of itself favours dissociation. It is readily intelligible, then, that the proportion of diatomic molecules in the vapour can at no temperature be sufficiently great to allow of their detection by the usual physico-chemical methods. In passing, for example, from vapour saturated at 277° C. to vapour saturated at

727° C., Pringsheim and Carrelli estimate that the proportion of diatomic molecules should increase only from 3 in 1000 to 2 in 100.

When a mixture of sodium and potassium vapours at 300° C. is illuminated with white light, the spectrum of the fluorescent emission comprises, besides the blue-green and red band systems characteristic of the sodium and potassium molecules themselves, another intense system of bands in the orange-yellow stretching from about 520 to 620 $\mu\mu$ and covering the D lines. Since these bands are absent or practically so from the fluorescence of the vapour of either pure metal, it appears probable that they originate from a K—Na complex, probably a diatomic KNa molecule. That the band system in the orange-yellow is in any case unconnected with the band systems of either pure metal has been shown by Pringsheim and Rosen (*loc. cit.*) from the characteristics of the resonance series which may be excited in K—Na mixtures with monochromatic light in the orange or yellow. Two such resonance series are excited by the two yellow lines of mercury at 5770 and 5791 Å, and both are represented by the progression formula

$$\nu = \alpha - 124{\cdot}8p + 0{\cdot}68p^2.$$

It follows from this that the first vibration quantum of the normal molecule concerned in the orange-yellow band system is about 124 cm.$^{-1}$, which is distinctly different from the first vibration quantum either of the normal Na_2 or of the normal K_2 molecule. If the above resonance formula can be regarded as at all accurate, the heat of dissociation of the supposed KNa molecule works out to about 16 kilo-calories, which is intermediate between the heats of dissociation of Na_2 and K_2.

As with sodium and potassium vapours, the vapours of rubidium and cæsium exhibit well-defined absorption band systems in the visible, but a detailed investigation of these or of the corresponding band fluorescence has not yet been carried out in either case. Rubidium vapour has, indeed, been found to give three distinct groups of fluorescence bands in the red, orange, and green when illuminated with white light, but only the system in the red appears to have its counterpart in the absorption spectrum of the pure vapour. In view of the fact that the metal nearly always contains traces of potassium and sodium, it is not unlikely that the band systems in the orange and green will be found to derive from molecules of these elements or from Rb—Na or Rb—K complexes.

Mercury.—At moderate temperatures and the corresponding saturation pressures (from about 1 mm. upwards), there appear in the absorption spectrum of mercury vapour, not only the absorption lines of the Hg atom at 2537 Å and 1849 Å, but also two fairly broad regions of apparently continuous absorption, the one region lying close to the 2537 Å line on its long wave-length side, the other covering the 1849 Å line. When the vapour under the same conditions is illuminated with light whose wave-length falls within either of these absorption bands, corresponding fluorescent emission is produced. The obviously close connection between these two regions of absorption and fluorescence and the two atom lines themselves naturally suggests that they derive from an unstable Hg_2 molecule, the energy levels of which differ but little from those of the atom. Such molecules would necessarily have to be very loosely bound, and in agreement with this they appear to be destroyed by higher temperatures, since the absorption regions in question disappear when the mercury vapour is superheated at constant pressure. From the diminution of the absorption with increasing temperature, Franck and Grotrian have indeed estimated the heat of dissociation of the hypothetical Hg_2 molecule as 1 kilo-calorie. The assumption of a loosely bound Hg_2 molecule as the absorbing unit is also consistent with the apparent absence of band or fine line structure in the absorption regions. An Hg_2 molecule would naturally have a very large moment of inertia, consequently the fine lines of each individual vibration band would be very closely packed; a loosely bound molecule would also have a very small separation of consecutive vibrational sub-levels, consequently the bands themselves would also run together and form an apparent continuum.

In addition to the above two regions of absorption and fluorescence, mercury vapour at moderately low pressures also absorbs and emits in a region between 240 and 210 $\mu\mu$ which is unconnected with any line of the atom spectrum. The fluorescent emission here has a definite band structure, so that for this region of absorption and fluorescence a different kind of molecule to that mentioned above is seemingly operative. Whether this molecule is a more stable modification of Hg_2 or whether it is a complex of Hg with some impurity has not yet been definitely settled.

Mercury vapour when illuminated at higher temperatures and saturation pressures with ultra-violet light gives a much more extensive system of fluorescence bands than above described, stretching from the ultra-violet through the visible and down to the red. This emission, which has been extensively studied within recent years by Wood, Rayleigh, and others, appears visually as a greenish luminescence. It appears to be conditioned by absorption on the part of the dense vapour within the already mentioned molecular absorption regions adjacent to the atom lines, but it can hardly be of the nature of simple molecular resonance, since mercury vapour does not itself absorb anywhere near the visible. Of the many interesting features of this fluorescence we may mention one which, though difficultly intelligible, nevertheless seems to be well authenticated, and must be very pertinent to the ultimate solution of the elementary processes which the emission entails. This is that a part at least of the fluorescent emission requires the continued distillation of mercury; the fluorescence of the vapour above liquid mercury is specially intense while the liquid is being heated, but when the liquid and vapour are both maintained at constant temperature, or when the saturated vapour itself is superheated, the visible luminescence practically vanishes.

THE EFFECT OF PRESSURE ON THE RESONANCE RADIATION OF GASES AND VAPOURS.

We have so far confined ourselves almost exclusively to the fluorescence of gases and vapours at very low pressures, thereby imposing a condition which ensures that the photoexcited units in the illuminated system are isolated during their natural life period. Under such conditions, spontaneous emission is the only possible fate for each excited unit, and the spectrum of the fluorescence contains only those lines which represent permitted transitions from the excited state to states of lower energy content. An optimum yield of fluorescence (reckoned as number of quanta emitted per quantum absorbed) is naturally expected in such circumstances, and this expectation has in fact been experimentally verified for one or two cases—notably for the D line and the 2537 Å line resonance of sodium and mercury vapours at pressures below 10^{-3} mm. Hg.

In the present Section we still restrict ourselves to the resonance radiation of monatomic and diatomic gases and vapours, but consider now the case when the originally excited atoms or molecules are not isolated within their natural life periods. This condition can be realised either by increasing the pressure of the fluorescing gas itself or by the addition to it of other gases or vapours. It is unnecessary to make more than a formal distinction between these two possibilities. When by either means the pressure of the system is raised to such a value that the average time between collisions becomes comparable with, or less than, the normal life of the photoexcited state, the possibility of inelastic collisions and radiationless quantum jumps on the part of the primarily excited units is introduced. It is our purpose now to examine what the effect of these will be on the nature and yield of the fluorescent emission of the system.

We have already become familiar with one kind of radiationless quantum jump in the excitation of atoms and molecules by inelastic collisions with fast moving electrons. Such processes, involving the transformation of kinetic energy of the colliding partners into internal energy of one of them, are called " inelastic collisions of the first kind." Klein and Rosseland (*Z. Physik*, **4,** 46, 1921), to whom this term is due, predicted on theoretical grounds that the reverse type of process—" inelastic collisions of the second kind "—should also be possible, whereby the energy of internal excitation of an atom or molecule can by its collision with an electron be transformed into energy of relative translatory motion. The two types of inelastic collision obviously illustrate a special case of the Principle of Microscopic Reversibility or Detailed Balancing which has acquired a fundamental significance within recent years. Inelastic collisions of either kind are not, however, confined to collisions between electrons and atoms or molecules, and the use of Klein and Rosseland's terms has been extended by Franck to include inelastic collisions taking place between atoms and molecules. Collisions of the first kind are in a general way responsible for the temperature luminescence of matter, collisions of the second kind for the degradation of radiant energy into energy of unordered heat motion. There are, however, various other possibilities of transformation and transfer of internal energy of excitation by collision which are included by Franck in the general category of " collisions of the second kind," and which are detailed below.

When optically excited atoms or molecules collide within their natural life period with other atoms or molecules, the collisions may be perfectly elastic, in which case the capacity of the illuminated system for emission is unaffected by the occurrence of the collisions. If some proportion of the collisions be inelastic, the extent to which the fluorescent emission is affected depends in the first instance upon the collision frequency and upon the efficacy of the collisions to bring about discrete changes in the internal energy content of the excited units. Depending upon the special circumstances of the case, however, various different types of inelastic collisions of the second kind are conceivable, agreeing only in the one particular that they all involve a quenching of the photoluminescence which would otherwise be obtained. If we denote the primarily excited atom or molecule by A^* and the collision partner by B, one possibility is that all the internal energy of A^* will be degraded to heat energy, or partly degraded and partly used for other purposes by B. Another possibility is that A^* may lose only a fraction of its total internal energy, and pass to a lower stationary state which may be labile or metastable. Again, A^* may be raised by the collision to a slightly higher labile or metastable state, the slight gain in its internal energy being at the expense of its own thermal energy and that of B. Finally, there exists the possibility that the photoactive unit A^* may react chemically with B, or that A^* may be dissociated by the collision through a redistribution of its total internal energy content. These last eventualities which may properly be included in the category of " collisions of the second kind " are, of course, of frequent occurrence in postulated mechanisms of photochemical action.

In the above, we have discussed the consequences of an inelastic collision of the second kind only in so far as it affects the primarily excited atom or molecule A^*. In addition, however, we must also consider the disposal of the energy which is liberated by the collision. When this is small it may in general be expected to appear as energy of translatory motion of the two colliding particles. In certain cases, however, B may have one or more internal energy levels lying below that of A^*. A transformation of part of the internal energy of A^* into internal energy of B is then conceivable. Depending upon the energy transfer and the nature of B, we may then obtain the emission of radiation characteristic of B (sensitised fluorescence), or B may suffer chemical decomposition or may react, by virtue of its excitation, with other atoms or molecules in the system (sensitised photochemical action). If these possibilities are excluded, the internal energy acquired by B will, of course, be degraded ultimately by collisions into energy of heat motion. All these different possible fates of the originally excited unit A* and of its collision partner B in inelastic collisions have been realised in practice by experimental investigations of the effect of different added gases upon the resonance radiation of atoms and molecules. The case where A* is an optically excited atom is, of course, the simplest both theoretically and practically, and corresponding to this the bulk of quantitative observations on collisions of the second kind have been carried out in systems containing mercury vapour at low partial pressure and illuminated with the 2537 Å resonance line.

Before proceeding to give a detailed account of the results of such observations, however, we must not forget to note that the addition of a foreign gas affects the resonance emission of a vapour in two different ways, (*a*) by altering the yield of resonance emission as above through the agency of collisions of the second kind, (*b*) by broadening the absorption line of the vapour. The pressure broadening of spectral lines has already been discussed in Chapter III. In relation to our present subject, the phenomenon of pressure broadening introduces the complication that in the presence of an added gas the illuminated vapour can possibly absorb more radiation from the illuminating beam, and thereby form more excited units, than in the absence of the gas. Thus it may happen that when the vapour is excited by a fairly broad absorption line the intensity of resonance emission will be increased instead of decreased by the addition of foreign gases. In illustration of this point, we may mention Wood's observations (*Phil. Mag.*, **44,** 1107, 1922; *Physikal. Z.*, **13,** 353, 1912) that the intensity of resonance emission of mercury vapour, excited at room temperature with the comparatively broad 2537 Å line from an uncooled mercury lamp, is greatly increased by the addition of a few millimetres of helium or argon. In the same circumstances, however, the presence of air or hydrogen diminishes the intensity of the resonance emission. The difference in these results must be taken to mean that helium and argon are relatively inefficient, compared with air or hydrogen, in deactivating excited mercury atoms by collision. The deactivating effects of the former gases are then more than compensated by the increased amount of absorption which they induce by broadening the absorption line, and a spurious increase in the intensity of resonance emission results. With air or hydrogen present, however, the increased absorption from the broad exciting line which they also produce is more than balanced by their ability to deactivate excited Hg atoms by collision.

From the above, it is evident that measurements of the intensity of resonance of a vapour in the absence and in the presence of a foreign gas are really not strictly comparable for purposes of computing the efficacy of the gas as a deactivating agent unless the measurements refer to exactly equal extents of optical excitation of the vapour in the two cases. In practice this condition is more or less realised by illuminating in both cases with the *narrow* resonance line of the pure vapour itself, obtained from another resonance tube at the same temperature and saturation pressure. The illuminated vapour with or without added gas absorbs over the whole width of this narrow line. This is the principle of the method employed by Stuart and by Mannkopff (see below) for measuring the quenching effects of different gases on the resonance emission of mercury and sodium vapours. Even with this method, however, the extents of optical excitation of the illuminated vapour in the presence and absence of added gas are not exactly equal, since the added gas decreases somewhat the absorption coefficient of the vapour for its own resonance line. Actually this decrease amounts to only a few per cent. for moderate pressures of added gas, and the slight decrease in fluorescence attributable to this is usually far outweighed by the decrease due to deactivation of the optically excited atoms by collisions.

Quenching Effects of Different Gases on the Resonance Emission of Mercury and Sodium Vapours.—The observations of Wood already referred to on the effects of air, hydrogen, helium, and argon on the 2537 Å resonance of mercury vapour are useless for the purpose of computing the true deactivating powers of these gases, since the exciting illumination used by Wood does not fulfil the criterion that it should be equally well absorbed by the mercury vapour in the presence and in the absence of added gas. Stuart (*Z. Physik*, **32,** 262, 1925) has, however, studied the quenching effects of different gases under strictly comparable conditions by always exciting the mercury vapour to resonance with the narrow resonance line of the pure vapour itself. The experimental method is illustrated by the accompanying diagram. The fairly narrow 2537 Å emission line of a water-cooled quartz mercury lamp L is used to excite the mercury vapour in the resonance tube R_1 to resonance (R_1 contains no added gas). A pencil of the fluorescent emission from R_1 excites the mercury vapour in R_2, and the intensity of the resonance emission from R_2 is measured by its blackening of the photographic plate P. Consecutive exposures are taken, varying the nature and pressure of the added gas in R_2. In order to obviate errors arising from irregularities in the source L, the blackening of each exposure on P is measured in terms of

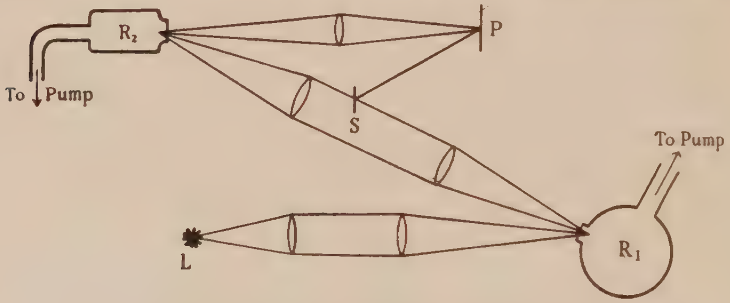

FIG. 37.—Diagrammatic representation of Stuart's apparatus.

the blackening simultaneously produced alongside by a definite fraction of the resonance pencil of radiation from R_1, which is reflected on to P by the mirror S. Both R_1 and R_2 are maintained at room temperature—about 18° C.

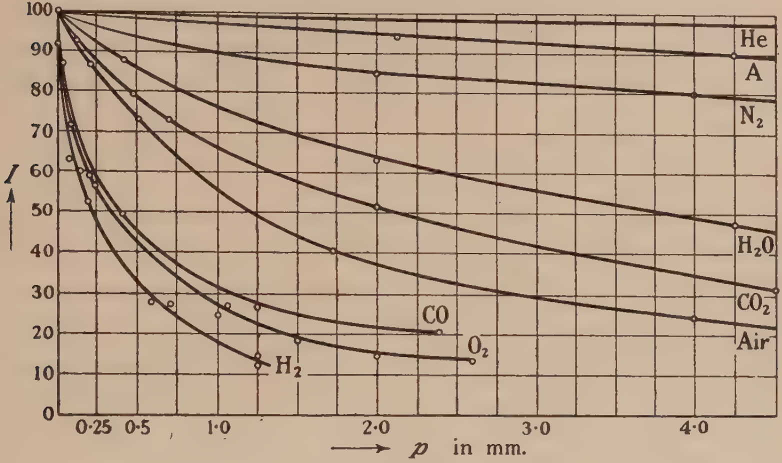

FIG. 38 (*a*).

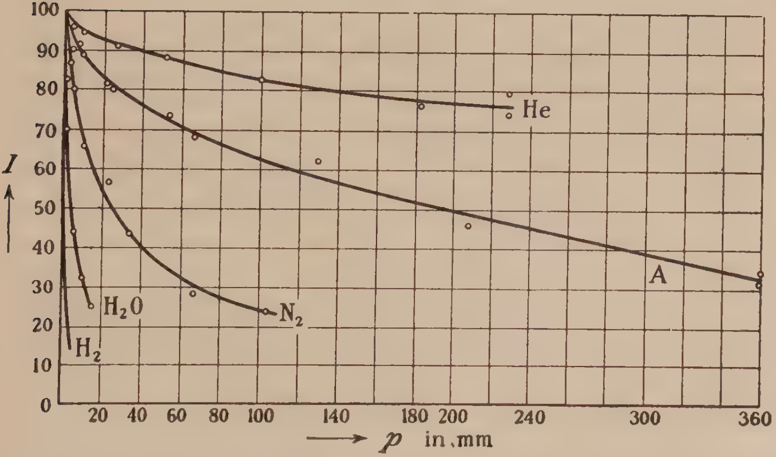

FIG. 38 (*b*).

Quenching of the resonance radiation of mercury vapour by added gases.

The results of Stuart's investigations are shown graphically in Figs. 38 (*a*) and 38 (*b*), where the yield I of resonance radiation from R_2 is plotted against the pressure of added gas. The values of I are given as percentages of the maximum yield I_0 of resonance radiation which is obtained without added gas.

The very great difference in the quenching efficiencies of the various gases used by Stuart can readily be appreciated from the graphs. The most effective gases are H_2, O_2, and CO, for each of which a pressure of less than 0·5 mm. suffices to reduce the yield of resonance radiation by one half. The least effective are the inert gases helium and argon. For the former gas, Stuart finds by extrapolation of the He curve of Fig. 38(*b*) that $p_{\frac{1}{2}}$, the pressure required to reduce the yield of resonance radiation I_0 by one half, is of the order of one atmosphere. The values of $p_{\frac{1}{2}}$ for the other gases used will be found in Table XXIX.

The quenching of the resonance radiation of mercury vapour by any added gas can only be due to collisions of the second kind suffered by the photoexcited Hg (2^3P_1) atoms during their normal life period, whereby these atoms suffer radiationless quantum jumps and are rendered incapable of re-emitting the 2537 Å line. Whether the inelastic collision transfers the Hg(2^3P_1) atom in each case to the normal state or only to a neighbouring metastable state is for the moment immaterial. It is evident, however, from Stuart's results that different gas molecules have very different probabilities of deactivating an Hg(2^3P_1) atom by colliding with it. If every collision between, say, a hydrogen molecule and an excited mercury atom results in the deactivation of the latter, the same obviously cannot be true for every collision between a helium or an argon atom and an excited mercury atom. The actual percentage of the total number of collisions between the molecules of any gas and Hg(2^3P_1) atoms which lead to deactivation is estimated by Stuart in the following way.

Stern and Volmer (*Physikal. Z.*, **20,** 183, 1919) have shown that, in the case where *every* collision between an optically excited atom and a gas molecule results in deactivation, the normal life τ of the excited atom (when isolated) equals the time $T_{\frac{1}{2}}$ between consecutive collisions of the excited atom and gas molecules at the pressure $p_{\frac{1}{2}}$ of gas which is necessary to reduce I_0 to half its value. If only the fraction x of collisions result in deactivation, however, the relation between τ and $T_{\frac{1}{2}}$ is

$$\tau = T_{\frac{1}{2}}/x \qquad . \quad . \quad . \quad . \quad (10)$$

Now the number ν of collisions per second which a particular Hg(2^3P_1) atom suffers with gas molecules is given, on the basis of the kinetic theory, by

$$\nu = 2(r_1 + r)^2 \, . \, n_1 \, . \sqrt{2\pi R\theta\left(\frac{M_1 + M}{M_1 M}\right)},$$

where n_1 is the number of molecules of the gas per c.c., θ is the absolute temperature, r_1 and r are the respective radii of the mercury atom and the gas molecule, and M_1 and M are their respective molecular weights. The average time T between consecutive collisions of the Hg(2^3P_1) atom with molecules of the gas is the reciprocal of ν. Changing from concentration to pressure units, it can easily be deduced from this that at 18° C. (291° absolute) the average time T between the consecutive collisions of a particular $Hg(2^3P_1)$ atom and the gas molecules at the pressure p of gas is given by

$$T = \frac{3{\cdot}835 \times 10^{-23}}{(r_1 + r)^2 . p} \sqrt{\frac{M_1 M}{M_1 + M}},$$

where the pressure p is in millimetres of mercury. This equation, together with equation (10), then gives the following relation between τ, $p_{\frac{1}{2}}$, and x:—

$$\tau . x = \frac{3{\cdot}835 \times 10^{-23}}{(r_1 + r)^2 . p_{\frac{1}{2}}} \sqrt{\frac{M_1 M}{M_1 + M}}. \qquad . \qquad . \quad (11)$$

Now an examination of Stuart's data shows that of the gases used by him, the fraction x must be greatest for oxygen. True, hydrogen is more effective than oxygen in quenching the resonance radiation, but a good part of hydrogen's efficiency derives from the much greater velocity of translatory motion of the hydrogen molecules, which give them the opportunity to collide more often with $Hg(2^3P_1)$ atoms than do oxygen molecules. Suppose, then, we assume that every collision between an excited mercury atom and an oxygen molecule deactivates the mercury atom ($x = 1$). Then, using $p_{\frac{1}{2}}$ for oxygen $= 0{\cdot}35$ mm., $M_1 = 200{\cdot}6$, $M = 32$, and the kinetic theory values $r_1 = 1{\cdot}75 \times 10^{-8}$ and $r = 1{\cdot}45 \times 10^{-8}$ cm. for the radii of the mercury atom and the oxygen molecule, the value of τ works out as $5{\cdot}7 \times 10^{-7}$ sec. This value of τ is, however, distinctly greater than the value 1×10^{-7} sec. which is given by several other methods (cf. Chapter III., p. 170) as the normal life of the 2^3P_1 state of the mercury atom, so that there appears to be some error in one or other of the assumptions made above. The error cannot, of course, lie in the assumption that x for oxygen is unity. A higher value of x is impossible, and a lower value of x leads to a still higher estimate for τ than the one already obtained. The only other magnitude open to question in the calculation is the radius r_1 of the mercury atom. The value of r_1 used above is the kinetic collision radius of the normal Hg atom, but the collision radius of the excited (2^3P_1) atom which should be employed is probably much higher than this. In agreement with this, the value of r_1 which is calculated from equation (11) with $x = 1$ for oxygen and $\tau = 1 \times 10^{-7}$ sec. is 6×10^{-8} cm., which is $3{\cdot}4$ times the collision radius of the normal mercury atom.

Using $r_1 = 6 \times 10^{-8}$ cm., the percentage efficiencies ($100x$) of various molecules in deactivating the Hg (2^3P_1) atom by collision are now easily calculated. The results are contained in Table XXIX. Too much stress need not be put upon the absolute or even the relative values of the x's in this table, since (*a*) the values are all calculated on the questionable basis that the collision radius of the $Hg(2^3P_1)$ atom is the same in every case, and (*b*) the effect of the added gas in decreasing the absorption is left out of account. This effect is negligible for the low pressures of H_2,O_2,CO,CO_2, and H_2O required to reduce the intensity of fluorescence to half its value, but it must be appreciable in the cases of N_2, A, and He, and therefore the estimates of x for these gases are likely to be too high. The results do demonstrate, however, the very great differences in the deactivating powers of H_2, O_2, and CO on the one hand and N_2, A, and He on the other. Practically every collision of an excited $Hg(2^3P_1)$ atom with one of the former molecules is a collision of the second kind, but rarely does a collision of an excited mercury atom with N_2, A, or He result in deactivation.

The quenching of the resonance radiation of pure mercury vapour at high temperatures and corresponding saturation pressures (cf. p. 249) must also be due to deactivating collisions between $Hg(2^3P_1)$ atoms and normal Hg atoms. The saturation pressure of mercury at 18° C. is only 0·001 mm., at which pressure the photoexcited atoms are practically isolated, but at temperatures above 100° C. and the corresponding saturation pressures above 0·3 mm., the photoexcited atoms collide with normal Hg atoms within their natural life period, and deactivation is then possible. Corresponding to this it is found that while the brightness of the resonance emission of mercury vapour, saturated at each temperature, at first increases with increasing temperature (due, of course, to the increasing absorption capacity of the vapour), a maximum brightness is reached at about 100° C., and above this the intensity falls off rapidly, being reduced to half the maximum brightness at 150° C., when the saturation pressure is 2·9 mm. From this it is evident that the efficiency of normal Hg atoms in deactivating photoexcited Hg atoms is fairly great; indeed, in view of the relatively small frequency of collisions of these heavy, slow-moving atoms with one another, a value of $p_{\frac{1}{2}}$ of 2·9 mm. must mean that practically every collision between a normal and an excited Hg atom deactivates the latter.

TABLE XXIX.

QUENCHING OF MERCURY RESONANCE RADIATION BY VARIOUS GASES AT 18° C.

Gas.	H_2.	O_2.	CO.	CO_2.	H_2O.	N_2.	A.	He.
$p_{\frac{1}{2}}$(mm. Hg) .	0·2	0·35	0·4	2·0	4·0	30	240	(760)
$T_{\frac{1}{2}} \times 10^8$ (sec.)	7	10	8	2	1	0·13	0·02	0·003
100x . .	70	100	80	20	10	1·3	0·2	0·03

Measurements similar to those of Stuart have been carried out by Mannkopff (*Z. Physik*, **36,** 315, 1926) on the damping of the resonance emission of sodium vapour at 200° C. by hydrogen, nitrogen, and helium-neon mixtures. The results are summarised in the accompanying table. The nitrogen molecule is most efficient in deactivating excited sodium atoms, and the efficiencies in the last row are computed on the assumption that x for nitrogen is unity. Taking the normal life of the excited 2^2P state of the atom as 10^{-8} sec., this requires that the collision radius of the excited atom is over four times the kinetic collision radius of the normal atom.

TABLE XXX.

QUENCHING OF SODIUM RESONANCE RADIATION BY VARIOUS GASES AT 200° C.

Gas.	H_2.	N_2.	He—Ne.
$p_{\frac{1}{2}}$(mm. Hg.) .	2·0	1·6	135
100x . .	50	100	1·7

From these results for mercury and sodium vapours, it is clear that the deactivating power of a gas is distinctly specific, not only to the nature of the gas itself, but also to the nature of the excited atom which it is required to deactivate. This is specially well illustrated by the efficiencies of nitrogen and hydrogen in quenching the resonance radiations of mercury and sodium vapours. Even for the same excited atom, however, there does not appear to be any simple relation between the deactivating power of a gas and any of its other physical properties such as its polar character or its electron affinity. In quenching the mercury resonance radiation, for example, the electropositive hydrogen is practically as effective as the electronegative oxygen, while the polar molecules of water vapour and carbon dioxide occupy an intermediate position between the non-polar hydrogen and oxygen and the equally non-polar inert gases.

It is, however, hardly legitimate to compare the quenching effects of different gases in this way without taking account of the possibility that the deactivation processes concerned may be very different in different cases, in respect both of the fate of the originally excited atom and of the use to which the energy liberated by the inelastic collision may be put. In the quenching of the resonance radiation of mercury vapour, for example, the quenching implies the destruction of the 2^3P_1 state of the atom, but there are three possible ways by which this can be effected :—

(1) the mercury atom may, after the collision, be left in the metastable 2^3P_0 state ;

(2) the atom may pass directly to the normal 1^1S_0 state ;

(3) the atom may enter into a stable or transient chemical union with the whole or part of the colliding molecule. The cumulative evidence of a number of investigations goes to prove that the deactivating collisions of the most effective quenching agents H_2 and O_2, and probably also CO, CO_2, and H_2O involve one or other of the possibilities (2) and (3). The least effective quenching agents N_2, A, and He merely transfer the 2^3P_1 atom to the metastable 2^3P_0 state.

In systematising these and other results of a similar character, the following rule is found to be of fairly general applicability :—

Those inelastic collisions are most probable of occurrence which involve only a small degradation of internal energy into kinetic energy of translatory motion.

This rule is specially pertinent to the low quenching efficiencies of the inert gases. These are monatomic and have no internal energy levels, electronic or vibrational, which could be attained by utilising all or part of the energy of an excited Hg or Na atom. In order that an inelastic collision should occur, it is therefore necessary that the whole of the liberated internal energy should appear as translational energy of the separating units, and according to our rule this event is of improbable occurrence. Correspondingly, the inert gases are found to be particularly inefficient in quenching both mercury and sodium resonance radiation, and in the case of the $Hg(2^3P_1)$ atom an inelastic collision with He or A, when it does occur, involves the least possible degradation of internal energy, namely the transformation $Hg(2^3P_1) \rightarrow Hg(2^3P_0)$, whereby only about 5000 calories of the total internal energy of the excited mercury atom is degraded. The di- and polyatomic gas molecules, on the other hand, have the faculty of taking up large quantities of available energy as internal energy of vibration, hence their greater quenching efficiencies, and hence also the fact that in the case of mercury vapour the deactivating action of these gases is more often $Hg(2^3P_1) \rightarrow Hg(1^1S_0)$ than $Hg(2^3P_1) \rightarrow Hg(2^3P_0)$. Other things being equal, the former transition, which is infinitely the more probable of the two as a spontaneous process, is likely to be the more probable also as a collisional process.

The case of nitrogen is in some respects anomalous, since this molecule should also have the capacity to take up large amounts of energy as vibrational energy, and should therefore be expected to be equally as efficient as the hydrogen or oxygen molecule in quenching the resonance emission of mercury vapour. Instead of this, however, the nitrogen molecule behaves to the excited Hg atom in much the same way as does an inert gas atom. Possibly the chemical inertness of nitrogen towards mercury has something to do with this, since it appears that the processes of deactivation of excited mercury atoms by hydrogen and oxygen are not entirely of a physical nature but involve some sort of chemical transformation. The available energy of the excited mercury atom is not, however, sufficient to dissociate the nitrogen molecule as it is to dissociate the hydrogen molecule, and the formation of a mercury-nitrogen complex is unlikely. On the other hand, neither hydrogen nor nitrogen can be dissociated by the excess energy of the excited $Na(2^2P)$ atom, yet the nitrogen molecule is 100 per cent. efficient and the hydrogen molecule is about 50 per cent. efficient in destroying the resonance emission of sodium vapour. It is possible that these high efficiencies are related to complex formation between the excited sodium atom and the colliding molecule, the complex retaining the whole of the excess energy until it is destroyed by a subsequent collision. The less than 100 per cent. efficiency of hydrogen in the case of sodium resonance has been related by Mannkopff to an observation of Wood, that when sodium vapour is excited in the presence of a small quantity of hydrogen by *one* of the D lines, the fluorescent emission contains *both* the D lines. From this it follows that not all inelastic collisions of the second kind between hydrogen molecules and excited sodium atoms reduce the excited atoms to the normal (1^2S) level, but an appreciable fraction of the collisions brings about the transformation $2^2P_1 \rightarrow 2^2P_2$, or *vice versa*. Such collisions would not, of course, affect the yield of resonance radiation as measured by Mannkopff, since in his measurement of the intensity of fluorescent emission the D_1 and D_2 lines were not separately distinguished.

The truth of the statement made above, that most if not all inelastic collisions of nitrogen molecules or inert gas atoms with Hg (2^3P_1) atoms transfer these to the metastable 2^3P_0 state, is clearly indicated by the results of Donat and Loria on the effect of these gases on the mercury-sensitised fluorescence of thallium vapour (cf. next Section). The same may be inferred, at least for the case of nitrogen, from Wood's observations (*Phil. Mag.*, **50**, 774, 1925) on the absorption and fluorescence of mercury vapour in the presence of this gas when illuminated with the full light of the quartz mercury lamp. Briefly, Wood finds that under these conditions the vapour absorbs not only the 2537 Å line characteristic in absorption of the normal atom, but also such lines as 4047 Å and 2967 Å which require the metastable state as the initial state in absorption. A very appreciable concentration of metastable 2^3P_0 atoms is therefore produced in the system by inelastic collisions of mercury atoms, primarily excited to the 2^3P_1 level by the absorption of the 2537 Å line, with nitrogen molecules. Quite low partial pressures of nitrogen suffice to make the 4047 Å line show up in the absorption; the line is first noticeable at $p_{N_2} = 0{\cdot}1$ mm. and is very strong at $p_{N_2} = 2$ mm. Corresponding to this absorption by metastable atoms in the system, the fluorescent emission under the same conditions contains, besides the resonance 2537 Å line, a number of other lines in the visible and near ultra-violet connoting spontaneous transitions of mercury atoms from the 2^3S, 3^3S, and 3^3D levels to the 2^3P levels. These lines also appear in the fluorescent emission of *pure* mercury vapour illuminated with the full light of the mercury arc (cf. p. 149), but with much feebler intensity, since in the pure vapour the levels 2^3S, etc. are only reached by the improbable event of two consecutive absorption processes *via* the labile 2^3P_1 state. Specially noteworthy in the fluorescence is the visible green line at 5461 Å which is intensified over thirty times by the presence of nitrogen at a pressure of about 2 mm. The different processes responsible for the excitation of this line in the presence and in the absence of nitrogen are indicated as follows :—

$$\begin{tikzcd}
\mathrm{Hg}(1^1S_0) \arrow[r, "2537\,\text{Å}"] & \mathrm{Hg}(2^3P_1) \arrow[dl, "\mathrm{N_2}"'] \arrow[d, "4358\,\text{Å}"] & \\
\mathrm{Hg}(2^3P_0) \arrow[r, "4047\,\text{Å}"] & \mathrm{Hg}(2^3S_1) \arrow[r] & \mathrm{Hg}(2^3P_2) + 5461\,\text{Å}.
\end{tikzcd}$$

The various stages can easily be followed on the energy diagram of the mercury atom given in Fig. 18.

Wood finds that helium and carbon monoxide also produce some intensification of the fluorescent lines $3^3D \rightarrow 2^3P$ obtained with mercury vapour under the above conditions of illumination. The effects are not so marked as with nitrogen, however, so that these gases are not as effective as nitrogen in transforming the labile 2^3P_1 atom to the metastable 2^3P_0 state. The lesser efficiency of helium is in conformity with its lesser efficiency—(cf. Table XXIX.)—in quenching the resonance radiation. Since, however, carbon monoxide is much more effective in the latter respect than nitrogen, Wood's result must mean that most, but not all, inelastic collisions between CO and Hg(2^3P_1) result in complete deactivation of the mercury atom.

Mercury-Sensitised Dissociation of Hydrogen.—The detailed nature of the inelastic collision between a hydrogen molecule and a photoexcited mercury atom is of special interest, in view of the large number of photosensitised reduction processes which are found to occur in systems containing mercury vapour and hydrogen when illuminated with the 2537 Å line. These photosensitised reactions are treated in detail in Chapter XI. Cario and Franck were the first to note (*Z. Physik*, **11,** 161, 1922) that when a mixture of mercury vapour and hydrogen is illuminated with the 2537 Å line, an active form of hydrogen is obtained. This reduces metal oxides at ordinary temperatures, it is strongly adsorbed on the walls of the containing vessel, and it has an abnormally large thermal conductivity (Senftleben, *Z. Physik*, **33,** 871, 1925), all of which properties Langmuir has shown to be characteristic of atomic hydrogen. Cario and Franck accordingly presumed that atomic hydrogen is formed by inelastic collisions between Hg(2^3P_1) atoms and hydrogen molecules, thus—

$$\mathrm{Hg}(2^3P_1) + \mathrm{H_2} \rightarrow \mathrm{Hg}(1^1S_0) + 2\mathrm{H}.$$

That such a dissociation can occur is evident from a comparison of the available energy of excitation of the Hg(2^3P_1) atom, viz. 112,000 calories, with the minimum energy of 100,000 calories required to split the hydrogen molecule into normal atoms. This is not, of course, the only conceivable way in which an excited mercury atom could be deactivated by a hydrogen molecule with formation of "active hydrogen." Two other possibilities have received special consideration by different workers, viz. (1) the formation of a mercury hydride HgH and a hydrogen atom, and (2) the formation of an excited hydrogen molecule; but the evidence in favour of either of these is at best inconclusive, and theoretical considerations suggest that, while all three modes of deactivation may occur simultaneously, the most probable of the three is likely to be that involving the simple dissociation of the hydrogen molecule into atoms (cf. p. 588). The difference between the deactivating processes involved in inelastic collisions of the Hg(2^3P_1) atom with hydrogen and with nitrogen is admirably illustrated by some recent experiments of Cario and Franck and of Meyer (*Z. Physik*, **37,** 619, 639, 1926). Repeating Stuart's measurements for hydrogen and nitrogen with the same partial pressure of mercury vapour as before (the saturation pressure corresponding to 18° C.) but now working at 750° C., Cario and Franck find that, while the quenching effect of hydrogen is the same at 750° as at 18° C., the quenching effect of nitrogen entirely disappears at the higher temperature. This result is interpreted as follows. While each inelastic collision of an Hg(2^3P_1) atom with a hydrogen molecule takes the atom to the 1^1S_0 state, each inelastic collision with a nitrogen molecule only changes the atom to the 2^3P_0 level which lies 0·2 volt or 5000 calories below the labile 2^3P_1 level. At the lower temperature, the metastable 2^3P_0 atom is subsequently completely deactivated by collision with a wall or with a molecule of impurity, accidentally present, such as hydrogen. At the higher temperature, however, before this complete deactivation can occur the metastable atom suffers a collision of the *first* kind with a fast-moving nitrogen molecule, whereby 5000 calories of translatory energy are transformed into internal energy, and the metastable atom is changed back to the labile state. In this way, the mercury atoms which at the higher temperature are deactivated by collisions of the second kind with nitrogen molecules, are not irretrievably lost for purposes of emission, as are those deactivated by collisions with hydrogen molecules.

Cario and Franck have further noted that at 750° C. hydrogen in the presence of nitrogen quenches the resonance emission of mercury vapour more powerfully than hydrogen alone. Since nitrogen itself does not quench the resonance emission at 750° C., this result must be taken to mean that not only do the hydrogen molecules completely deactivate the labile (2^3P_1) atoms with which they collide (the normal quenching effect), but they also completely deactivate any metastable atoms previously formed by inelastic collisions of labile atoms with nitrogen molecules, and thus effectively prevent the re-transformation of these metastable atoms into labile atoms by collisions of the first kind. The fact that Hg(2^3P_0) atoms are very unstable to collisions with hydrogen molecules is independently attested by Dorgelo's observation (*Physica*, **5,** 429, 1925) that the life of the metastable state, which in pure mercury vapour at low pressures is about $\frac{1}{200}$ sec., is reduced below the limit of measurement by the presence of a trace of hydrogen. The same conclusion is to be drawn from Meyer's observation that at ordinary temperatures the rate of the photosensitised dissociation of hydrogen into atoms in the system (Hg vapour, H_2, 2537 Å) is considerably increased, for low partial pressures of hydrogen, by the addition of an excess of nitrogen. Since, in the presence of nitrogen, the number of dissociating collisions between hydrogen molecules and Hg(2^3P_1) atoms must be diminished rather than increased, the increased yield of hydrogen atoms can only be explained on the assumption that some Hg(2^3P_1) atoms, which might otherwise revert to the normal state by spontaneous emission before colliding with hydrogen molecules, are " fixed " in the metastable 2^3P_0 state by collision with nitrogen molecules. In this state they persist till they collide with hydrogen molecules, whereupon they are completely deactivated and the hydrogen molecules are dissociated. The excess energy of the metastable mercury atom is 4·7 volts or 107,000 calories, which is more than sufficient to effect the dissociation of the hydrogen. In Meyer's experiments, then, the nitrogen, while decreasing the stationary concentration of labile (2^3P_1) atoms in the illuminated system, nevertheless increases the gross stationary concentration of excited ($2^3P_1 + 2^3P_0$) atoms which can dissociate hydrogen molecules by inelastic collisions. From his results, Meyer calculates that the metastable mercury atoms must be practically as efficient as the labile atoms in causing the dissociation of hydrogen.

SENSITISED FLUORESCENCE.

This phenomenon, when realised under sufficiently simple conditions, affords the most direct physical evidence of transfer of internal energy from one atom or molecule to another by inelastic collisions. A system containing atoms or molecules of two different species is illuminated with radiation which only the one species A can absorb, yet the fluorescent emission may contain lines or bands characteristic of the other species B. In order that this should be possible, not only is energy transfer by collision from A to B necessary, but it is in general also necessary that B should possess one or more labile levels of excitation below the photoexcited level of A. We may therefore expect that, as a rule, the frequency of the sensitised emission will be less than that of the exciting light. Exceptions to this are found at high temperatures, which must be interpreted to mean that the colliding units possess enough thermal energy, in addition to the optically derived internal energy of A, to raise B to still higher energy levels.

The process of sensitised fluorescence must often be operative, without the fact being appreciated, in the photoluminescence of mixtures and solutions, whether gaseous, liquid, or solid. The occurrence of the phenomenon in circumstances where the exact nature of the energy transfers can be readily appreciated was first detected by Cario and Franck (*Z. Physik*, **10,** 185, 1922 ; **17,** 202, 1923) in mixtures of mercury vapour with other metal vapours. Cario found that when a mixture of mercury and thallium vapours is illuminated with the mercury resonance line 2537 Å, which the mercury but not the thallium atoms can absorb, the fluorescent emission contains, besides the 2537 Å line itself, a number of lines characteristic of thallium—notably the thallium green line 5350 Å. Suitable pressures of the two metal vapours for the observation of the effect are obtained by heating the metal thallium by itself to about 800° C. in the excitation tube, and supplying the mercury vapour from a side tube wherein mercury is independently heated to 100° C. This gives a mixture of mercury and thallium vapours at about 0·3 and 2 mm. respectively. The spectrum of the sensitised fluorescence of thallium as observed by Cario and Franck contains the thallium lines indicated in the following table:—

TABLE XXXI.

SENSITISED FLUORESCENCE SPECTRUM OF THALLIUM VAPOUR AT 800° C.

Line.	Origin.	Excitation Potential.	Intensity.
3776 Å	$2^2S \rightarrow 2^2P_1$	3·3 volts	Strong.
5350	$2^2S \rightarrow 2^2P_2$		Strong.
2768	$3^2D \rightarrow 2^2P_1$	4·5 ,,	Weak
3529	$3^2D \rightarrow 2^2P_2$		Very Strong.
2580	$3^2S \rightarrow 2^2P_1$	4·8 ,,	Weak.
3230	$3^2S \rightarrow 2^2P_2$		Very Strong.
2826	$4^2S \rightarrow 3^2P_2$	5·3 ,,	Weak.
2920	$4^2D \rightarrow 3^2P_2$	5·2 ,,	Weak.
2709	$5^2D \rightarrow 3^2P_2$	5·5 ,,	Very Weak.

Since the photoexcited mercury atom which by collision excites the thallium atom to emission has 4·9 volts excess energy, the presence of the first six lines in the sensitised fluorescence calls for no comment. The appearance of the lines deriving from the 4^2S, 4^2D, and 5^2D levels of the thallium atom, however, requires that in their case thermal energy of translatory motion must also be utilised for the collisional excitation. In the case of the lines 2826 and 2920 Å, the additional amounts of energy required are 7000 and 9000 calories, and many pairs of thallium and Hg(2^3P_1) atoms colliding at 800° C. must possess such a quantity of translatory energy. For the 2709 Å line, however, the additional energy available at collision must be 14,000 calories. Corresponding to the infrequency of occurrence of this event, the line 2709 Å, while perceptible, is very weak in the sensitised fluorescence compared with the others.

The intensity relations of the first three pairs of lines given in the above table are interesting. The excitation levels 3^2S and 3^2D of the thallium atom lie very close to the excitation level 2^3P_1 of the mercury atom, hence the inelastic collisions of normal thallium with Hg(2^3P_1) atoms which leave the thallium atoms in either of these states involve very little degradation of energy, and should therefore be the most probable of occurrence. In agreement with this the lines 3529 and 3230 Å which derive from the 3^2S and 3^2D levels respectively are the strongest lines in the observed fluorescence spectrum. That the lines 2768 and 2580 Å which derive from these same levels are weak by comparison is due to the fact that these, as distinct from the former pair, are absorption lines of the normal thallium atom (cf. p. 144). Hence these lines, though probably as often emitted within the system as the 3529 and 3230 Å lines, are to a great extent absorbed before emerging. The pair of lines 3776 and 5350 Å originate from the 2^2S state of the thallium atom. In its excitation to this level by collision with an Hg(2^3P_1) atom, 1·6 volts or 37,000 calories of the total available energy is not utilised and must appear as energy of translatory motion of the separating units. This event should be of less frequent occurrence than the excitation of the thallium atom to the 3^2S or 3^2D levels, and correspondingly the 5350 Å line is found to be less strong in the emission than either the 3529 or the 3230 Å line. The high intensity of the 3776 Å line, which like the 2768 and 2580 Å lines is also an absorption line of the normal thallium atom, and should therefore be weak in the emerging fluorescence, is due to the fact that the excited 2^2S thallium atoms which emit it all possess abnormally high velocities of translatory motion. The emission line is therefore very much broadened, and only the central portion of it is absorbed before it leaves the excitation tube.

Cario and Franck have also investigated the fluorescence, sensitised by mercury vapour, of silver, zinc, and cadmium, and the similarly sensitised fluorescence of lead, bismuth, indium, and the alkali metal vapours has been observed by other workers. The results of these observations are very similar to those detailed above for thallium-mercury systems; the excitation level of the other atom which is most readily attained by inelastic collision with the photoexcited mercury atom is that which necessitates the minimum degradation of internal energy.

We pass on now to a brief mention of the effects of added gases upon the mercury-sensitised fluorescence of thallium. The effects of nitrogen, argon, and hydrogen have been investigated by Donat (*Z. Physik*, **29,** 345, 1924) and also by Loria (*Physical Rev.*, **26,** 573, 1925). It is found that both nitrogen and argon, which slightly weaken the resonance emission of mercury vapour itself, greatly enhance the yield of sensitised fluorescence from a thallium-mercury vapour mixture illuminated with the 2537 Å line. Argon is somewhat more effective in this respect than nitrogen. Hydrogen, however, which markedly weakens the resonance emission of mercury vapour, also decreases the yield of sensitised fluorescence, the intensity of the resonance radiation and that of the sensitised fluorescence both falling off in much the same way with increasing partial pressure of hydrogen. This effect of hydrogen is readily intelligible, since the hydrogen molecule colliding with a photoexcited mercury atom completely deactivates it with the result that fewer thallium atoms can be excited by collision with Hg(2^3P_1) atoms. Further, certain excited thallium atoms which contain energy sufficient to dissociate the hydrogen molecule may also be deactivated by collision before they emit, and it is possibly due to this that the intensities of different lines of the sensitised fluorescence are somewhat differently affected by the same pressure of hydrogen. The enhancing effects of argon and nitrogen are ascribed by Donat to the fact that inelastic collisions of photo-excited mercury atoms with these molecules only transfer the mercury atom to the metastable state, in which it still possess 4·7 volts of excess internal energy. This metastable mercury atom is presumably insensitive to subsequent collisions with argon or nitrogen molecules, hence the presence of one or other of these gases increases the gross stationary concentration of excited Hg ($2^3P_1 + 2^3P_0$) atoms in the system. Both types of excited mercury atoms are, however, capable at the working temperature 800° C. of exciting thallium atoms by inelastic collision to the 2^2S, 3^2S, or 3^2D state, and so an increased yield of sensitised fluorescence is obtained.

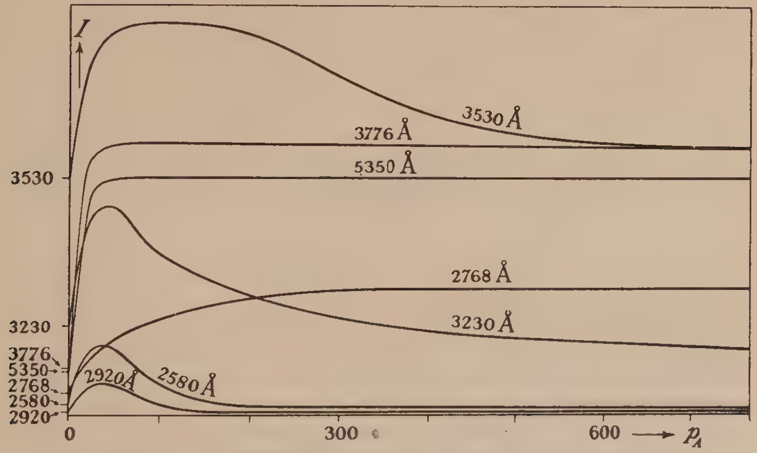

FIG. 39.—The effect of addition of argon upon the sensitised fluorescence of thallium vapour. (p_A = partial pressure of argon in mm. Hg.)

The presence of an atmosphere of argon results in a six-fold increase in the brightness of the thallium green line 5350 Å. Other lines, however, are not affected to the same extent; in fact, the variations of the intensities of the individual lines with increasing argon pressure are rather complex. The data of Fig. 39 are due to Donat (*loc. cit.*). By reference to Table XXXI. it will be seen from the figure that, with increasing pressure of argon, the intensities of most of the lines deriving from the higher 3^2S, 3^2D, and 4^2D energy levels of the atom first increase rapidly, but pass through maxima and then gradually fall off, whereas the intensities of the two lines 5350 and 3776 Å deriving from the 2^2S level rapidly increase to a steady value. This behaviour can in some measure be understood by considering that the 2^2S thallium atom must be very insensitive to collisions with argon atoms, since its deactivation would entail a large degradation of internal into translatory energy. On the other hand, the higher 3^2S, 3^2D, and 4^2D levels of the atom may be fairly unstable to such collisions, since their destruction does not necessarily entail a transition to the 2^2P_1 or 2^2P_2 level, but only to one of the intermediate levels 2^2S, 3^2S, or 3^2D, with a comparatively small degradation of energy. On this basis, the intensities of the lines deriving from these higher levels of the thallium atom should first increase with increasing pressure of argon, due to increase in the number of activating collisions of normal thallium atoms with excited mercury atoms, but at high pressures of argon this might be more than balanced by the increased frequency of occurrence of collisions with argon atoms which deactivate the excited thallium atoms.

We may conclude with a few remarks concerning the stability of the metastable (2^3P_0) mercury atom to collisions. The results of Cario and Franck and of Meyer (cf. p. 285) indicate that most collisions of this atom with hydrogen molecules deactivate it with simultaneous dissociation of the hydrogen molecule. On the other hand, Donat's results on the influence of argon and nitrogen on the mercury-sensitised fluorescence of thallium require for their explanation a very pronounced stability of metastable mercury atoms with respect to collisions with argon and nitrogen. An equally remarkable stability with respect to collisions with normal mercury atoms has been demonstrated by Orthmann and Pringsheim (*Z. Physik*, **35**, 626, 1926) in the following way. The experiments of Cario and Franck on the sensitised fluorescence of thallium-mercury vapour systems were repeated with a constant partial pressure of thallium vapour and a variable pressure of mercury vapour from 3 mm. upwards. It was found that while the 2537 Å resonance line disappears completely from the fluorescent emission at pressures above 90 mm., certain of the sensitised fluorescence lines of the thallium persist with great intensity, even at a partial pressure of mercury of 800 mm. This result must mean (*a*) that at high pressures the photoexcited mercury atoms are changed to the metastable state by collision with normal mercury atoms, and (*b*) that these metastable atoms survive an exceedingly large number of collisions with normal mercury atoms before they collide with thallium atoms to which they can transfer their excess energy. At $p_{\text{Tl}} = 0{\cdot}02$ mm., $p_{\text{Hg}} = 800$ mm., where a large yield of sensitised fluorescence is still obtained, each excited mercury atom must suffer more than ten thousand collisions with other mercury atoms before it encounters a thallium atom.

EFFECT OF ADDED GASES UPON THE RESONANCE AND FLUORESCENCE SPECTRA OF IODINE VAPOUR.

We will consider first the case where the vapour is illuminated by monochromatic radiation within the visible band system, so that all the primarily excited molecules attain the same higher energy level (n'', p'', m''). From this level, as we have seen, they revert in the absence of collisions to the normal electronic level with emission of a simple resonance series or progression of doublets. Now an optically excited molecule affords many possible modes of deactivation by inelastic collision compared with an excited atom, since the electronic, vibrational, and rotational states of the excited molecule can all be modified independently of one another. Depending upon the exact nature of the deactivation process which is preferred, an added gas may therefore be expected to have very different effects upon the resonance spectrum. Let us first suppose that the only type of inelastic collision which is operative is that which reduces the photoexcited molecule to its normal electronic state. In this case, the nature of the resonance spectrum should not be affected by the added gas, but the intensity of every line of the resonance series should progressively diminish with increasing pressure of the gas. It is, of course, immaterial from the point of view of the fluorescence whether a change of p and m is linked up with the change of n in the deactivation process here considered, since the deactivated molecule no longer emits any radiation. We take now the opposite extreme where the inelastic collisions cause a change only in the vibrational and rotational states of the photoexcited molecule, leaving it, however, in the same electronic state as before. The molecule, after the collision, is still capable of emitting. If, by the collision, only the value of m'' is altered, the molecule can now emit a progression of doublets belonging to the same " primary " bands as do the original resonance doublets, but differing from these in respect of the exact position of each doublet and also in respect of the value of the doublet separation $\Delta\nu$, which depends (cf. equation 7) upon the absolute value of the rotational quantum number of the emitting molecule. Since even large changes in m'' involve only a slight transformation of internal (rotational) into translatory energy, it may be expected that collisions, even if otherwise ineffective, will nearly always alter m'', and different collisions by different amounts. With gradually increasing pressure of added gas we should, therefore, anticipate a gradual transformation of each doublet of the original resonance series into a more or less complete band. Simultaneously with change of m'', however, a change in the vibrational quantum number p'' of the photoexcited molecule may also occur upon collision. In this event, the added gas should not only alter the original progression of resonance doublets into a progression of bands, but also introduce into the fluorescence spectrum other progressions of bands deriving from partially deactivated molecules with different values of p''. The alteration in p'' by collision will usually, though not inevitably, be a decrease, so that the new progressions of bands should on the whole be displaced from the " primary " progression in the direction of longer wave-lengths.

These effects of collisions upon the rotational and vibrational states of the photoexcited iodine molecule are admirably illustrated by the observations of Wood and Franck (*Phil. Mag.*, **21,** 265, 1911) on the nature of the fluorescence spectrum of iodine vapour produced by the Hg 5462 Å line in the absence and in the presence of helium. Helium happens to be a gas which is comparatively ineffective in completely deactivating the photoexcited iodine molecule by collision. In the absence of added gas, the fluorescence spectrum consists of the simple resonance series of doublets already described (p. 259). A pressure of 2 mm. of helium, however, suffices to transform each doublet into an almost complete band, and simultaneously to introduce between these " primary " bands a number of bands of other progressions deriving from vibrational energy levels of the emitting molecule different from that originally excited. At this pressure of helium the " primary " bands are still the most intense, but with 10 mm. of helium present this preferential emission has completely disappeared and the " primary " bands are no longer to be distinguished from the other bands in the now very complex fluorescence spectrum. While these changes in the nature of the spectrum are being brought about, the position of maximum intensity gradually shifts from the green towards the red, indicating that the originally excited iodine molecules are being more and more frequently and effectively robbed, before they emit, of vibrational energy by collisions. The gross intensity of the unresolved fluorescence is not, however, very much diminished by the presence of 10 mm. of helium, that is to say, only a small fraction of the inelastic collisions are such as to reduce the excited iodine molecules to their normal electronic level.

The opposite extreme is represented by chlorine. Wood and Franck find that the presence of a few millimetres of this gas considerably reduces the intensity of emission of the resonance series of iodine, but causes practically no transformation of the resonance lines into bands, and introduces no new lines or bands into the fluorescence spectrum. This pronounced difference in the effects of chlorine and helium must clearly be interpreted to mean that practically every inelastic collision of a photoexcited iodine molecule with a chlorine molecule results in complete deactivation, whereas practically every inelastic collision with a helium atom only alters the rotational and vibrational states of the excited molecule.

Argon, nitrogen, hydrogen, and oxygen are found by Franck (*Verh. deut. phys. Ges.*, **14**, 419, 1912) to produce, like helium, a change in the nature of the fluorescence spectrum. With increasing electronegative character of the added gas, however, this change in the nature of the spectrum is less and less pronounced and is replaced by an increasing efficiency of extinction of the total emission. Evidently for these gases some inelastic collisions deactivate completely, some only alter the vibrational and rotational states of the photoexcited molecule.

Wood and Franck (*Phil. Mag.*, **21**, 309, 314, 1911) have also studied the effects of the presence of various gases on the fluorescence of iodine vapour which is excited by *white light*. The fluorescence produced by this means in the absence of added gas is already a complex band spectrum (cf. p. 259), and, depending upon whether complete or incomplete deactivation of the photoexcited molecule is preferred, the main effect of an added gas is either to diminish the total intensity of fluorescence or to displace the whole fluorescence spectrum towards the red. The quenching effects of various gases, as represented by the pressures $p_{\frac{1}{2}}$ required to reduce the gross intensity of emission to half the original value, are given in the following table (see also Fig. 40) :—

TABLE XXXII.

QUENCHING OF THE FLUORESCENCE OF IODINE VAPOUR BY ADDED GASES.

Gas.	A.	H_2.	Air.	CO_2.	Ether.	Cl_2.	I_2.
$p_{\frac{1}{2}}$(mm.Hg) .	7	6	2·1	1·2	0·3	0·2	0·2

The value of $p_{\frac{1}{2}}$ for iodine itself is obtained by comparing the intensities of fluorescence of the vapour, *reduced to equal amounts of radiation absorbed*, at different vapour pressures. Qualitatively, at least, these data give the order of efficiency of the various gases in reducing the photoexcited iodine molecule to the non-fluorescing normal state by inelastic collisions, and there appears from them to be a distinct relationship between deactivating efficiency in this sense and the electronegative character of the added gas. It is further clear from the values of $p_{\frac{1}{2}}$ for chlorine, ether vapour, and iodine vapour itself that practically every collision must be effective in these cases. The data for the other gases can hardly be compared quantitatively since, in the photometric measurements from which they are derived, no account

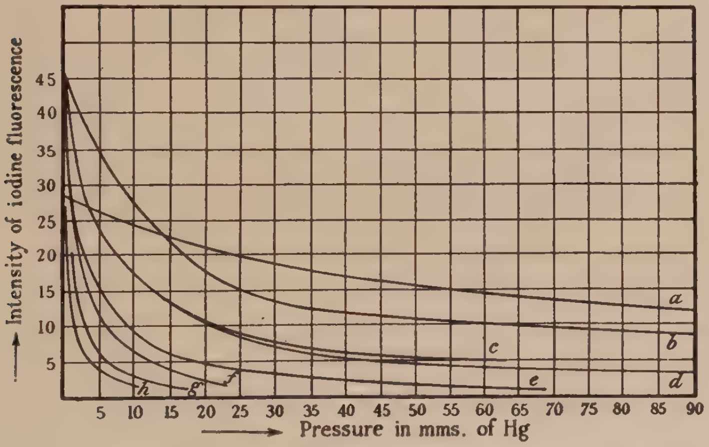

FIG. 40.—Quenching of the fluorescence of iodine vapour by added gases.
(*a*) helium (red); (*b*) helium (green); (*c*) argon; (*d*) hydrogen; (*e*) air; (*f*) carbon dioxide; (*g*) ether; (*h*) chlorine.

is taken of the change in the distribution of intensity with wave-length which these gases cause simultaneously with quenching. For each gas the green portion of the fluorescence spectrum is weakened to a greater extent than the red. This difference is most marked in the case of helium, for which independent photometric measurements in the green and in the red show that $p_{\frac{1}{2}}$ (green) = 15 mm., $p_{\frac{1}{2}}$ (red) = 65 mm. In order to obtain a true measure of the quenching effect of helium on the fluorescence of iodine vapour, it would obviously be necessary to determine the number of quanta of radiation of all frequencies which are emitted as a function of the pressure of added helium.

Ramsauer (*Z. Physik*, **40,** 675, 1927) has investigated whether oxygen (which quenches the general fluorescence of iodine vapour nearly as effectively as carbon dioxide) exerts the same quenching effect on (*a*) different resonance series, and (*b*) different lines of the same resonance series. The quenching effect is found to be practically the same for different series, from which it may be inferred that the probability of deactivation of the photoexcited iodine molecule by collision with an oxygen molecule is the same whatever the vibrational and rotational states of the excited molecule may be. On the other hand, Ramsauer finds that the individual lines of any particular resonance series are affected to a different extent by the same pressure of added oxygen. As a general rule the longer wave-length terms of the resonance series are weakened less than the shorter wave-length terms. Since all the terms of the one resonance series derive from the same state of excitation of the emitting molecule, it appears from this result that the intrinsic probability of occurrence of any spontaneous quantum jump in the molecule must depend to some extent on its environment. This effect, if substantiated, would have to be allowed for in any exact estimation of the yield of inelastic collisions from intensity measurements.

Turning now to the ultra-violet resonance series of iodine vapour which are excited by monochromatic illumination with light of wave-length below 200 $\mu\mu$, Oldenberg (*Z. Physik*, **25,** 136, 1925) finds that the effects of added gases on these series are quite different from their effects on the visible resonance series. Nitrogen and helium, which transform any visible resonance series of iodine vapour into a complete band system, merely produce a quenching of the ultra-violet resonance lines without the introduction of any new lines or bands which would indicate a change by collision of the rotational or vibrational state of the photoexcited molecule without simultaneous change of the electronic state. Concurrently with this, there occurs a quenching of the diffuse fluorescence bands lying between 200 $\mu\mu$ and the visible which always accompany the ultra-violet resonance series in emission. As previously mentioned, these diffuse bands probably correspond to some stage in the return (other than by direct reversal) of the photoexcited iodine molecule to the normal state. One peculiar effect of added gases upon the ultra-violet fluorescence of iodine is the development of a broad region of emission at about 346 $\mu\mu$. This emission is practically absent from the fluorescence of the pure vapour itself, but it is present in the emission spectrum of iodine vapour through which an electrical discharge is passed. For various reasons which we need not detail here, Oldenberg associates this emission with the recombination of positive and negative iodine ions to form the neutral molecule. Presumably these ions are themselves formed from photo-excited iodine molecules by collision with the molecules of the added gas.

FLUORESCENCE OF ORGANIC COMPOUNDS.

Photoluminescence of matter in the gaseous state of aggregation appears to be confined to certain of the chemical elements themselves, to the simpler types of inorganic compounds, and to a few organic compounds belonging chiefly to the aromatic group. This restriction need not necessarily possess any special theoretical significance; it may simply mean that it is practically impossible to obtain the vast majority of chemical substances in the vapour state under such conditions of temperature and pressure that an appreciable extent of absorption of radiation is possible without the occurrence of chemical decomposition, thermal or photochemical, or the degradation of the absorbed energy by collisions of the photoexcited molecules with other molecules before they re-emit. Examples of photoluminescence are much more numerous in the liquid state and especially in liquid solution, and here, strangely enough, the occurrence of a sensible amount of fluorescence appears to be conditioned by complexity rather than simplicity of structure of the absorbing molecule. The elements themselves and the simpler inorganic compounds do not fluoresce in the pure liquid state or in liquid solution—in fact, so far as inorganic substances are concerned, fluorescence in the liquid state is practically confined to the uranyl salts in aqueous solution.* Again, there are very few recorded cases of the fluorescence of simple aliphatic organic compounds, as against several hundreds of examples of the fluorescence of aromatic compounds, both in the pure liquid state and also when dissolved in suitable solvents. The great disparity between the numbers of recorded cases of fluorescence in the aliphatic and in the aromatic groups may, however, be due, at least in part, to experimental difficulties of observation of the effect, since in general the regions of selective absorption of aliphatic compounds (and therefore presumably their regions of fluorescent emission) lie much further into the ultra-violet than those of aromatic compounds.

Although organic substances have been examined in respect of their capacity for photoluminescence chiefly in the liquid and solid states of aggregation, and especially in liquid and solid solution, nevertheless a number of aromatic compounds have been tested within recent years for fluorescence in the vapour state, in most cases with positive results. Before dealing with specific cases, however, it will be convenient to make some general observations on the nature of the absorption and emission spectra of organic compounds in their different states of aggregation. The absorption spectra of the vapours of benzene itself and its simpler derivatives are band spectra of essentially the same type as that of iodine vapour. The fluorescence spectra of the vapours are also band spectra, and the fluorescence bands belong to the same system as the absorption bands. This is not to say that the fluorescence spectrum is simply the reversal of the absorption spectrum in each case. On the contrary, the " centre of gravity " of the fluorescence spectrum lies well to the long wave-length side of that of the absorption spectrum, the two overlapping slightly so that a few of the shorter wave-length fluorescence bands coincide with the longer wave-length absorption bands. This displacement of the emission spectrum relative to the absorption spectrum is readily intelligible when it is remembered that the bands in absorption must derive from the lowest vibrational sub-levels of the normal state of the molecule, whereas the bands in emission connect various photoexcited states with a whole range of vibrational sub-levels of the normal state. The same displacement is apparent in the fluorescence of iodine vapour, in particular, the major part of each resonance series excited by monochromatic illumination lies to the long wave-length side of the exciting line. It may be well to remark here that practically no work has been carried out so far on the photoluminescence of organic vapours excited at low pressures with monochromatic light, so that it is impossible to say whether under these circumstances resonance series might be obtained as in the case of many diatomic vapours at low pressures. The fluorescence spectrum of an organic vapour above referred to is that which is produced by illumination of the vapour at moderate pressures (at least several mm. Hg) either with white light or with monochromatic light of any wave-length which falls within the region of selective absorption of the vapour. Even with monochromatic illumination, the fluorescence spectrum at moderate pressures is a complete band spectrum. Each band is fully developed, and moreover the spectrum contains a great number of bands which derive from vibrational sub-levels of the upper state of excitation of the molecule other than the particular sub-level which is first attained by the primary act of absorption. Further, the distribution of intensity within the system of fluorescence bands appears to be entirely independent of the wave-length of the exciting light, so that between the act of absorption and that of emission a statistical equilibrium appears to be established in respect of the distribution of the primarily excited molecules among the various possible vibrational sub-levels of the main electronic level concerned. It may be recalled that the same "complete" fluorescence spectrum is obtained by monochromatic illumination of iodine vapour at low partial pressures of iodine but with a few millimetres of helium simultaneously present. In this case, the distribution of the primarily excited iodine molecules among a number of upper vibrational sub-levels previous to the act of emission results from inelastic collisions of the photoexcited molecules with helium atoms. Either this same kind of partially deactivating collision occurs in the case of the photoexcited organic vapour at moderate vapour pressures, or possibly the complex organic molecule has some mechanism whereby it can effect internal energy adjustments without the assistance of collisions. The latter possibility could only be adequately tested by examining the nature of the fluorescence excited in organic vapours by monochromatic illumination at pressures sufficiently low to ensure the absence of collisional effects. On the other hand, the fact that organic vapours fluoresce appreciably at moderately large pressures, where every photoexcited molecule must suffer a very large number of collisions with normal molecules during its natural life period, must mean that, even if inelastic collisions which transfer the photoexcited molecule from one vibrational sub-level to another do occur, collisions which would result in the complete deactivation of the excited molecule are relatively infrequent. The same lack of sensitivity of the excited molecule of an organic compound to collisions is, of course, indicated when the substance fluoresces also in the liquid state or in liquid solution. In either case, the collision frequency is enormously enhanced.

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* The phenomena here observed are exceedingly complex and can hardly be viewed in their proper perspective without a detailed correlation with the remarkable photoluminescence which the uranyl salts emit in the pure crystalline state. For a comprehensive account of this branch of our subject, the reader is referred to Nichols and Howes, *Fluorescence of the Uranyl Salts* (Carnegie Inst. of Washington, 1919).

The vapour spectra—absorption and emission—of benzene and its substitution compounds are very similar to one another in general structure and in spectral position, but a complete resolution of the spectrum into a system of individual vibration bands is possible only in the case of benzene itself and a few of its simpler derivatives, e.g. toluene, xylene, aniline, phenol. For these simpler molecules the totality of bands, when spectrally resolved, segregate more or less into a number of groups which probably represent different sequences of bands. With increasing weight and complexity of the substitution radicle or radicles, however, we obtain, in place of a number of groups of resolvable bands, a number of fairly broad regions of selective continuous absorption or emission, and for very complex molecules the absorption or fluorescence spectrum of the vapour consists simply of one or two broad continuous bands.* These continuous regions of selective absorption or emission encountered in the spectra of complex organic compounds must not be interpreted, as in the case of diatomic molecules, to mean dissociation or ionisation of the absorbing or emitting unit concerned. They result as indicated from the coalescing of groups of diffuse vibrational bands, due presumably to a lack of sharpness of definition of the vibrational energy levels of the molecule. Such poor definition of the vibrational sub-levels is probably to be referred to the intrinsic complexity of structure of the molecule which possesses very many internal degrees of freedom of vibration, rather than to any disturbing effects of neighbouring molecules.

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* The word *band* is unfortunately employed in spectroscopic work to denote both the individual vibration band of an electronic band system and also any broad continuous region of selective absorption or emission. When there is any doubt as to the meaning which might be attached to the word, a more complete specification is desirable.

The general structure of the vapour spectra of organic compounds is to a large extent preserved in the absorption and emission spectra characteristic of the liquid and solid states of aggregation, but many of the finer details are lacking. Even for the simplest compounds, individual bands are rarely observed; more usually the whole system of bands which are separable in the vapour spectrum coalesces in the case of the liquid or solid to give a continuous spectrum with several sub-maxima of absorption or emission, corresponding roughly in position to the groups into which the individual bands in the vapour spectrum segregate. For more complex molecules, one broad continuous band with a single broad maximum may be obtained. The relationship in position between the regions of absorption and fluorescence which holds for the vapour spectra persists for the denser states of aggregation, so that the continuous region of fluorescence lies to the long wave-length side of the region of absorption, usually with comparatively little overlapping. The coalescence in liquid and solid spectra of the individual bands or band groups into broad continuous regions of absorption or emission is most probably due to the very large and variable effects upon the quantised energy levels of the individual molecule which the fields of its close packed neighbours can exert. It is significant that the absorption or emission spectrum of the pure solid at very low temperatures often approaches in detail of structure the corresponding spectrum of the vapour itself. At low temperatures the effects of neighbouring molecules must still be considerable, but, as a result of the very much reduced extent of thermal agitation of the molecules, the variability of the effects in passing from molecule to molecule in the crystal lattice is much less pronounced.

The Photoluminescence of Benzene.—The ultra-violet absorption of benzene vapour has been examined by different workers, in most detail, however, by Henri (*J. Phys. Radium*, (6), **3,** 181, 1922; cf. also *Structure des Molécules* (Paris, 1925)). According to Henri, the complete absorption spectrum divides into three main parts, (1) a region of absorption bands, which exhibit rotational fine structure, between 270 and 220 $\mu\mu$, (2) a region of narrow but continuous (predissociation) bands between 220 and 205 $\mu\mu$, and (3) a broad region of continuous absorption beginning at 205 $\mu\mu$ and stretching further into the ultra-violet. Only the first region need interest us here, since apparently wave-lengths beyond 220 $\mu\mu$ do not produce fluorescence in the vapour. The spectrum between 270 and 220 $\mu\mu$ consists of a series of eight band groups, each with a fairly sharply defined short wave-length limit which is a sub-maximum of absorption. The positions of these short wave-length limits are given in the second column of Table XXXIII. Each group of bands contains several individual members, and each of these in turn exhibits under high dispersion a rotational fine structure. In attempting a quantum analysis of this band system, Henri has assumed that the totality of bands between 270 and 220 $\mu\mu$ comprises two independent systems corresponding to transitions of the normal benzene molecule in absorption to two different upper states of electronic excitation. Kronenberger and Pringsheim have, however, pointed out (*Z. Physik*, **40,** 75, 1926) that the facts hardly justify such an assumption. On their view, all the bands belong to the same system, and only one degree of freedom of vibration in the molecule is assumed to be operative, in contrast to the three degrees of freedom of vibration involved in Henri's classification of the bands. Kronenberger and Pringsheim regard the band groups as simple sequences, all the bands in any particular group corresponding to the same change $(p'' - p')$ in the vibration quantum number but to different initial values of p'. The band groups themselves are (in the wave-number scale) practically equally spaced with an average separation $\Delta\nu \approx 922$ cm.$^{-1}$; the individual bands of each group are also equally spaced with $\Delta\nu \approx 80$ cm.$^{-1}$. Accordingly, the positions of all the bands are found to be represented to a very fair degree of approximation by the empirical equation

TABLE XXXIII.

ABSORPTION AND FLUORESCENCE SPECTRA OF BENZENE IN VARIOUS STATES OF AGGREGATION AT ORDINARY TEMPERATURES.

(λ's of short wave-length limits of band groups.)

n.	Vapour.		Liquid or Solid.		Dilute Solution in Alcohol.	
	Abs.	Fl.	Abs.	Fl.	Abs.	Fl.
+ 6	2275		2297		2290	
+ 5	2324		2339		2330	
+ 4	2363		2385		2378	
+ 3	2416		2432		2428	
+ 2	2471		2488		2485	
+ 1	2528	2541	2550		2547	
0	2589	2602	2608		2598	2599
− 1	2667	2667	2689	2686	2681	2679
− 2		2739		2761		2754
− 3		2815		2837		2827
− 4		2895		2920		2910
− 5		2980				3005
− 6		3065				

$$\nu = 38{,}600 + 922n - 80p$$
$$(n = -1, 0, +1, +2 \ldots;\ p = 0, 1, 2, 3 \ldots).$$

To obtain the significance of the terms in this equation, it is only necessary to neglect the squared terms in the theoretical equation (27) of Chapter IV. for the band system, and write the simplified equation in the sequence form

$$\nu = \nu_0 + \beta''(p'' - p') - p'(\beta' - \beta'').$$

Identifying the empirical sequence constant n with $(p'' - p')$ and the sequence variable p with p', it follows that $\beta'' = 922$ cm.$^{-1}$ and $\beta' - \beta'' = 80$, or $\beta' = 1002$ cm.$^{-1}$. Hence the vibration quanta of the normal and excited benzene molecules are about 1000 and 920 cm.$^{-1}$ respectively.

The band fluorescence of benzene vapour was first studied by McVicker and Marsh (*J.C.S.*, **123,** 820, 1923), and later by Reimann (*Ann. Physik*, **80,** 43, 1926). The spectrum which is excited at moderate vapour pressures by absorption within the 220 — 270 $\mu\mu$ absorption range is also a band spectrum consisting of several groups of bands with the same internal spacing $\Delta\nu = 80$ cm.$^{-1}$ as the groups in the absorption spectrum, and also with practically the same spacing $\Delta\nu = 920$ cm.$^{-1}$ of the groups themselves. The fluorescence band system lies, however, to the long wave-length side of the absorption system, so that the two spectra overlap only in so far as the three shortest wave-length groups of fluorescence bands coincide in position with the three longest wave-length groups of absorption bands. From Table XXXIII. it may be seen that the other fluorescence groups form a natural continuation of the series of absorption groups in the direction of increasing wave-length; in fact, the empirical formula given above suffices for both the absorption and the fluorescence bands, the fluorescence groups being, however, represented mainly by negative values $-1, -2, -3, \ldots$ of the sequence constant n.

Fig. 41 gives a diagrammatic representation of the complete system of fluorescence bands excited with the full radiation of a quartz mercury vapour lamp. It will be remarked that the strongest band groups in emission are those corresponding to $(p'' - p') = n = -1, -2, -3,$ and -4. The groups $(p'' - p') = n = 0$ and $+1$ are relatively very weak, and in particular the shortest wave-length bands of these two groups (at 2589 Å and 2528 Å respectively) which are specially strong bands in absorption are entirely absent in the fluorescent emission. These two bands are the members of their respective groups for which p or $p' = 0$, that is, they derive in absorption from the normal vibrationless state of the benzene molecule. Their absence from the fluorescence spectrum is probably due to their being reabsorbed by the vapour before emergence from the system (self-absorption). On the other hand, the shortest wave-length band 2667 Å of the $n = -1$ group in absorption is very intense in the fluorescent emission. This band corresponds in absorption to the normal molecule which already possesses one quantum of vibrational energy. Such molecules are comparatively few in number in the vapour at ordinary temperatures, so that there is little likelihood of this band being reversed in emission.

It is interesting to note that the ultra-violet fluorescence spectrum of benzene vapour is practically identical with the emission spectrum which is obtained when a high frequency (Tesla) discharge is passed through the vapour at moderate pressures. The latter spectrum contains the same eight groups of bands as are found in the fluorescence, and the individual bands themselves are identical as regards their wave-lengths in the two cases. There are, however, minor differences between the two spectra as regards the distribution of intensity among the bands and groups. For details of the method of excitation of the very characteristic "Tesla luminescence" spectra of organic vapours, the reader must be referred to a series of papers by Marsh, Stewart, and co-workers (*J.C.S.*, **123,** 642, 817, 2147, 1923; **125,** 1743, 1924; **127,** 999, 1925).

As already mentioned, the distribution of intensity in the fluorescence spectrum given by benzene vapour at moderate pressures is

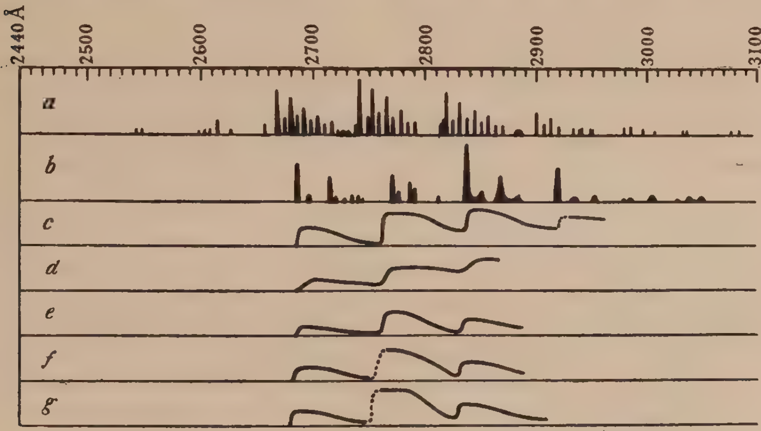


FIG. 41.—Fluorescence spectra of benzene excited by white light.

(*a*) vapour; (*b*) solid at − 180° C.; (*c*) solid at 0° C.; (*d*) liquid at 0° C.; (*e*) 30 per cent. solution in alcohol; (*f*) 12 per cent. solution in alcohol; (*g*) 4 per cent. solution in alcohol.

completely independent of the wave-length of the exciting light. Pringsheim and Reimann (*Z. Physik*, **29,** 115, 1924; *Ann. Physik*, **80,** 43, 1926) find, however, that at pressures below 1 mm. Hg, the nature of the spectrum which is obtained with monochromatic excitation alters. Only a few of the complete system of bands are now developed, and the particular bands appearing in each group depend upon the exciting wave-length employed. There does not, however, appear to be any very definite relationship between the frequencies of these bands and that of the exciting light, such as holds in the case of a resonance series. The addition of a few millimetres of a foreign gas, at constant partial pressure of benzene, serves to transform the incomplete fluorescence into the complete band spectrum which is characteristic of higher vapour pressures of benzene. From this it appears certain that the latter spectrum owes its fully-developed structure to the occurrence of inelastic collisions between normal and excited benzene molecules which transfer the photoexcited molecules to vibrational sub-levels different from that attained under monochromatic illumination by the primary act of absorption.

As regards the possibility of complete deactivation of the photoexcited molecule by collision, the benzene molecule is in this respect fairly sensitive to collisions with molecules of the strongly electronegative gases, but surprisingly insensitive to collisions with normal benzene molecules themselves. Thus an increase in the vapour pressure from 25 to 360 mm. only transforms the volume fluorescence of the vapour into surface fluorescence without altering appreciably the total intensity of emission for constant intensity of the exciting beam. The fluorescence persists also in the pure liquid, although with very much diminished intensity, so that the spectral range of the liquid fluorescence effectively covers only the three or four most intense groups of bands in the vapour fluorescence.

The fluorescence spectra of the vapour and the liquid also differ from one another in that the emission spectrum of the liquid consists, not of groups of separable bands, but of three or four regions of selective continuous emission. Each of these continuous regions agrees roughly in position with a group of bands in the vapour spectrum, but the short wave-length limit of each continuous region is slightly displaced from that of the corresponding group of bands towards the direction of longer wave-lengths. Details of structure are also absent from the absorption spectrum of the pure liquid, which likewise consists of a series of sub-maxima of absorption corresponding roughly in position with the groups of bands in the absorption spectrum of the vapour. The longest wave-length absorption band coincides with the shortest wave-length fluorescence band, and, in effect, the fluorescence spectrum forms a natural continuation of the absorption spectrum just as for the case of the vapour.

The spectra of the absorption and photoluminescence of the pure solid at ordinary temperatures are very similar in nature to those of the pure liquid. The fluorescence of the solid is, however, much more intense than that of the liquid, and the short wave-length edges of the fluorescence bands are much more sharply defined. A very marked change occurs in the nature both of the absorption and of the emission spectrum of solid benzene when the temperature is reduced to that of liquid air (— 180° C.). Under these conditions each continuous region of selective absorption or emission again breaks up, as in the case of the vapour state, into a number of separate narrow bands. The solid and vapour spectra differ, however, in the details of the distribution of intensity among the individual bands. Moreover, the short wave-length limits of the low temperature band groups practically coincide with the short wave-length edges of the continuous absorption and fluorescence bands of the solid and liquid at ordinary temperatures, so that for the denser states of aggregation there is always a slight displacement of the entire spectrum towards the direction of longer wave-lengths.

Table XXXIII. and Fig. 41, which is taken from the paper of Reimann already referred to, summarise the details of the photoluminescence of benzene in its different states of aggregation. The last three spectra of Fig. 41 show the positions of the three strongest fluorescence bands of benzene in alcoholic solution at different concentrations (ordinary temperatures). Other weaker bands which have been observed by Dickson (*Z. wiss. Phot.*, **10**, 167, 1912) in the fluorescence of benzene in dilute alcoholic solution are given in the table. It will be noted that while the bands in solution are of the same continuous nature as in the pure liquid, the short wave-length limit of each band moves slowly towards the visible with increasing concentration of benzene in the solution. This displacement of the spectrum towards the red with increasing concentration of the solute is a general characteristic both of the absorption and of the fluorescence of organic substances in solution. The main difference between the fluorescence of benzene in the pure liquid state and in solution lies, however, in the intensity. Starting with the pure liquid, which fluoresces very feebly, and gradually adding alcohol, the specific intensity of fluorescence of the system (referred always to the same amount of light energy absorbed) first increases very rapidly, but reaches a maximum value when the solution contains about 12 per cent. of benzene, and then remains practically independent of the concentration on further dilution. From this it appears certain that the photoexcited benzene molecule is decidedly more stable to collisions with alcohol molecules than to collisions with benzene molecules themselves. A more detailed consideration of the specific effects of the solvent medium upon the fluorescence of organic compounds in solution is given in a subsequent Section.

Other Organic Compounds.—The fluorescence spectra of the vapours of a large number of aromatic compounds—phenols, ethers, and amines—which are fairly easily volatilised have been examined by Marsh and co-workers (*J.C.S.*, **123**, 3315, 1923; **125**, 418, 2123, 1924). For the simpler derivatives of benzene, such as toluene, phenol, *p*-cresol, anisole, and *p*-toluidine, a definite band structure is observable in the vapour spectrum, and when observed, these "bands" agree roughly as regards their spacing with the band groups of benzene. Marsh remarks that of the di-substituted benzene derivatives, the *para*-compounds are always characterised by the most definite banding. With increasing number and complexity of the substitution radicles, the band structure gradually fades out of the spectrum. Thus the very definite banding in the fluorescence spectrum of aniline vapour is entirely absent from those of di-methyl and di-ethyl aniline and also from those of *ortho*- and *meta*-toluidine. Regular banding is again observed, however, in the case of *para*-toluidine.

Reimann (*Ann. Physik*, **80**, 43, 1926) has compared the capacities for fluorescence of the xylenes and the cresols in the pure liquid and solid states. As in the case of benzene, the solid spectrum is practically the same as the liquid spectrum at the same temperature (liquid supercooled for comparsion), but the very feeble fluorescence of the supercooled liquid is greatly intensified on crystallisation.

The fluorescence of benzene derivatives has been most extensively studied in solution, in which state the capacity for fluorescence is certainly most pronounced. Special reference may be made to the work of Dickson (*Z. wiss. Phot.*, **10,** 166, 181, 1911) and of Ley and Engelhardt (*Z. physikal. Chem.*, **74,** 1, 1910) who have carried out a detailed correlation of the absorption and fluorescence spectra of a very large number of aromatic compounds in alcoholic solution. So far as these spectra exhibit any band structure, the relationship between the absorption and emission systems of bands is the same as in the case of benzene itself. It may be remarked, however, that while the absorption and fluorescence spectra of the simpler derivatives of benzene lie, like those of the parent substance, in the ultra-violet, the replacement of the H's in the benzene molecule by alkyl, hydroxyl, amino, carbonyl . . . radicles always has the effect of displacing the complete spectral domain towards the visible. The same shift occurs in passing from benzene to naphthalene and anthracene. For the latter substance, although the selective absorption is still confined to the ultra-violet, the fluorescence, which in agreement with Stokes' Law always lies to the long wave-length side of the absorption, already stretches well into the visible. In Table XXXIV. are given the approximate limits of the fluorescence spectra of various representative aromatic substances in the vapour state and in alcoholic solution.

TABLE XXXIV.

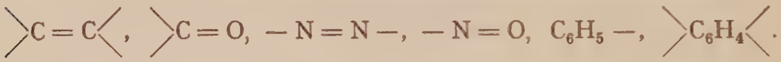
Substance.	Fluorescence in Vapour State.	Fluorescence in Alcoholic Solution.
Benzene . . .	254-335 $\mu\mu$	260-291 $\mu\mu$
Toluene . . .	267-335	262-289
o-Xylene . . .	267-341	260-313
Phenol . . .	276-347	286-364
Cresols . . .	282-368	286-385
Aniline . . .	296-391	300-410
p-Toluidine . .	306-368	323-398
Benzoic Acid . .	—	313-392
Anthranilic Acid .	—	366-490
Naphthalene . .	—	300-366
Naphthylamine .	338-450	370-530
Anthracene . .	390-432	366-435

The great displacing effect of the NH_2 group, as evidenced by comparing the spectral limits for benzene with those for aniline, or those for naphthalene with those for naphthylamine, is specially noteworthy. A comparison of the details of internal structure of the band absorption and fluorescence of benzene and its simpler derivatives leaves no room for doubt that the seat of the elementary processes of absorption and emission in these substances is always located in the benzene ring. Speaking in terms of the chromophore theory of absorption (see later) which has been developed by the organic chemist to take account of the relation between colour and chemical constitution, the benzene ring plays the part of the " chromophore " in this class of compound. The substitution radicle which displaces the spectrum towards the visible is similarly the " auxochrome." From the data of the above table it is seen that the amino group is a specially strong auxochrome in relation to the benzene chromophore. The displacing effect of any substitution radicle upon the positions of selective absorption and emission must of course be referred ultimately to an effect of its presence upon the strength of the particular valency bond in the molecule which is excited by the act of absorption. While various auxochromes can, from existing optical data, be arranged roughly in order of their displacing effects, it is, however, impossible in the present state of our knowledge to discuss the results quantitatively with any feeling of confidence. No doubt it will ultimately be possible from absorption and fluorescence measurements to construct and compare the energy diagrams of the simpler organic molecules and relate the energy levels intelligibly to their chemical structures.

Dyestuffs.—The most interesting examples of photoluminescence of organic compounds relate to the complex dyestuffs which absorb in the visible part of the spectrum. The possibility of fluorescence of these substances in the vapour and pure liquid states has as yet been very little investigated. The dyestuff itself is usually solid at ordinary temperatures, but, unlike the simpler aromatic compounds, the pure solid itself very seldom luminesces. In the dissolved state, however, most of the organic dyes appear to be capable of re-emitting the radiation which they absorb provided a suitable choice of solvent medium is effected. For the commonly investigated cases, of which we may cite fluorescein, eosin, æsculin, rhodamine, rhodulin, and chlorophyll, photoluminescence is observed whether the solvent medium is liquid or solid ; but for many other dyestuffs, such as malachite green, phenolphthalein, purpurin, methyl violet, methyl blue, etc., the re-emission of the absorbed radiation appears to be possible only in solid solution.

The regions of visible absorption and emission of the fluorescent dyestuff in solution at ordinary temperatures are broad and continuous, usually overlapping one another to some slight extent, and together covering such a spectral range as we normally associate with a complete band system. Within the regions of continuous absorption and emission there are often definite sub-maxima or at least traces of sub-maxima, the evidence in embryo of band structure. There is never sufficient detail of structure, however, in the absorption and emission spectra to permit of the same unequivocal correlation of the two spectra as is possible in the case of benzene and its simpler derivatives. The organic dyestuffs have in the past played an important part in the development of theories which attempt to connect the absorption and fluorescence capacities of organic compounds with special structural features of the molecules concerned. Two separate problems are here involved, (*a*) the identification of the particular group or linkage in the molecule which is primarily responsible for the act of absorption, (*b*) the correlation of the ability of the molecule to re-emit the radiation which it absorbs with the presence in it of other special groups or linkages. While recognising the importance of these fundamental questions, it is impossible within the limits of a few pages to give more than a rough idea of the lines along which their solution has been approached.

The great differences which exist between the capacities of different types of organic compounds to absorb selectively in the visible and ultra-violet were early recognised to depend primarily upon the presence or absence in the molecules of definite groups, radicles, or linkages. These colour-controlling units are termed *chromophores*, and the molecule which contains one or more chromophores is called a *chromogen*. Among the most important chromophores are the following :—



$$>C=C<, \quad >C=O, \quad -N=N-, \quad -N=O, \quad C_6H_5-, \quad >C_6H_4<.$$

ethylene, carbonyl, azo, nitroso, phenyl, quinonoid.

We may recall that the phenyl group acts as the chromophore in the selective absorption of benzene and a great number of its simpler derivatives in the ultra-violet. The mode of identification of the chromophore unit in any particular molecule may be simply illustrated by taking the case of the azo group, which is held responsible for the colour (visible absorption) of a large body of aromatic compounds, including many dyes. In azobenzene ($C_6H_5-N=N-C_6H_5$), which is coloured a deep orange-red, there might appear to be some doubt as to whether the phenyl group or the azo group is responsible for the visible absorption. This doubt is at once resolved, however, when azobenzene is compared with hydrazobenzene ($C_6H_5-NH-NH-C_6H_5$) or diphenyl ($C_6H_5-C_6H_5$) or diphenylmethane ($C_6H_5-CH_2-C_6H_5$), all of which are colourless.

While the presence or absence of a chromophore decides whether or not the molecule will exhibit selective absorption, the spectral position of the absorption band which is introduced by each chromophore group depends upon the nature of the remainder of the molecule. Thus, although azobenzene is orange-red in colour, progressive substitution by methyl of the phenyl groups in the molecule gives methane azobenzene and azomethane which are yellow and colourless respectively. More exactly expressed, the azobenzene absorption band lies practically entirely in the visible with a maximum of absorption at 450 $\mu\mu$, whereas that of methane azobenzene lies partly in the visible and partly in the near ultra-violet with maximum at 410 $\mu\mu$, and that of azomethane lies wholly in the ultra-violet with maximum at about 350 $\mu\mu$. We see from this that the juxtaposition of a phenyl radicle (itself a chromophore) and the azo group has the effect of displacing markedly the region of selective absorption (which is properly ascribed to the azo chromophore) towards the visible. Numerous other examples of such displacement, which is characteristic of the "conjugation" of chromophores in the molecule, might be cited. Thus, acetone which contains only one carbonyl chromophore is colourless and absorbs only in the ultra-violet (270 $\mu\mu$), whereas diacetyl and triketopentane absorb sensibly in the visible, being yellow and orange-red respectively. A similar gradation in colour is obtained in passing through the series benzophenone (colourless), benzil (yellow), diphenyltriketone (golden yellow), diphenyltetraketone (red). In order that the two chromophore units may exert an appreciable effect upon one another, juxtaposition is, however, necessary. If other non-chromophoric groups intervene, the spectral region of absorption is usually not very different from that of the compound which contains only one chromophore. For example, acetylacetone and acetonylacetone, although both possess, like diacetyl, two $>C = O$ chromophores, are nevertheless colourless; in fact, absorption measurements show that the region of selective absorption of acetonylacetone is practically identical with that of acetone itself. It may be remarked in relation to the conjugation of chromophores that the phenyl and quinonoid radicles, which are usually regarded as unit chromophores, are really composite in character. Among aromatic compounds the quinonoid linkage is one of the chief colour-producing chromophores.

Selective absorption bands are displaced towards longer wavelengths, not only by the conjugation of chromophores in the molecule, but also (though to a relatively less extent) by coupling with the chromophore of one or more groups or radicles which of themselves are not considered to possess chromophoric properties. Such groups are termed *auxochromes*. We have already noted the displacing effects of various auxochromic radicles upon the absorption and fluorescence bands of benzene. In general, amino groups appear to be the most effective auxochromes, especially effective when the H's of NH_2 are replaced by heavier alkyl radicles. Hydroxyl and alkoxyl groups come next in order, and the alkyl groups themselves are only very feeble auxochromes. The specific effect of any auxochrome, however, depends to some extent upon the nature of the chromophore or chromophores with which it is associated, and also upon the nature of other auxochromes which may be simultaneously coupled with the chromophore, so that it is hardly permissible to formulate general rules for their action.*

The systemisation of the regions of selective absorption of organic compounds in terms of the chromophore theory has proved of valuable service to the organic chemist for the elucidation of chemical structure, in particular, for the detection of such structural changes in the molecule as are represented by keto-enol or phenyl-quinonoid tautomerism. It should be remarked, however, that the distinction which the theory draws between chromophores and auxochromes is most probably one of degree rather than of kind. The usually recognised chromophore groups all contain residual affinity, that is, they represent the weak links in the organic molecule. When this residual affinity is saturated, the chromophoric power is lost and the group or linkage becomes an auxochrome. This, however, must merely mean that the valency electrons in the auxochrome group are much more firmly bound than those in the chromophore, and their optical excitation now involves regions of selective absorption lying outside the convenient range of visible and near ultra-violet wave-lengths.

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* For details the reader may be referred to Smiles, *The Relations between Chemical Constitution and some Physical Properties* (Longmans, 1910), or Kauffmann, *Beziehung zwischen physikalischen Eigenschaften und chemischer Konstitution* (Enke, Stuttgart, 1920).

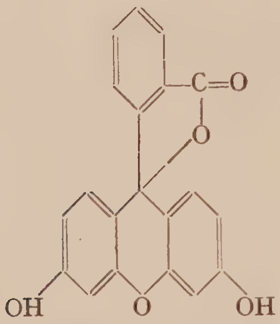
Turning now to fluorescence, it is of course axiomatic in the light of modern theory that, for true fluorescence, that part of the molecule which is directly concerned in the act of absorption must also be the seat of the fluorescent emission. From the fact, however, that many complex organic compounds absorb strongly in the visible but give no trace of visible fluorescence, attempts have been made in the past to connect the capacity of a substance to re-emit the radiation which it absorbs with the possession of certain special structural features. The most interesting of such attempts is that of R. Meyer, who in 1897 carried out an extensive survey of the visible fluorescence of numerous aromatic compounds in liquid solution and concluded that visible fluorescence always depends upon the presence in the molecule of a special *fluorophore* group, distinct from the chromophore group which is held responsible for the primary absorption. The Meyer fluorophores are all six-membered rings, the principal of which are the pyridine, azine, oxazine, and pyrone rings. As an example of how Meyer traced the function of these groups, we may take the case of the pyrone ring.

Both fluorescein and eosin (tetrabromfluorescein) contain this ring as part of their structure, and both these substances, which give coloured solutions when dissolved in alkali, exhibit a very strong visible fluorescence when illuminated with visible light. On the other hand, phenolphthalein, which is structurally identical with fluorescein except for the fact that the bridge oxygen which forms the pyrone ring in the latter substance is missing (cf. the structural formulæ on p. 310), gives no trace of visible luminescence, although its alkaline solution is also strongly coloured. *o*-Cresolphthalein and α-naphtholphthalein also give coloured solutions in alkaline media but do not fluoresce, whereas *p*-cresofluorane, α-naphthofluorane, and β-naphthofluorane, which are the anhydrides of the corresponding phthaleins and again contain the pyrone ring, give strongly fluorescent solutions when dissolved in concentrated sulphuric acid.

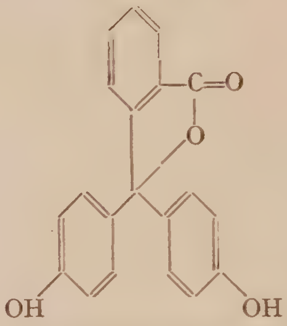
The fluorophoric action of the pyrone ring is not, however, confined to the members of the fluorane group. The same ring was held responsible by Meyer for the occurrence of visible fluorescence in the rhodamine group of dyestuffs, in xanthone and its derivatives, and in diphenylpyrone. It may be remarked that in all these instances the pyrone ring is flanked by heavy atom complexes, benzene or substituted benzene rings. According to Meyer, this was to be regarded as a further condition for the functioning of the fluorophore in the molecule. Thus diphenylpyrone fluoresces strongly in concentrated sulphuric acid solution, whereas neither dimethylpyrone nor γ-pyrone itself gives any trace of visible fluorescence under the same conditions.

The original fluorophore theory of Meyer has been considerably modified since its inception, and it is now generally recognised that the function of such special groups as the pyrone ring in promoting visible fluorescence is of a more subsidiary character than was at one time imagined. The presence of such a grouping in the molecule certainly cannot be regarded as a necessity for fluorescence in general, since (*a*) benzene and its simpler derivatives which do not contain any of these special groups fluoresce in the ultra-violet, and (*b*) the more complex organic compounds, whether or not they contain a Meyer fluorophore and whether or not they fluoresce in the visible, also give a short wave-length fluorescence. Thus, of the two substances fluorescein and phenolphthalein which are both coloured in alkaline solution, only the first emits as a result of the absorption in the visible, but both substances absorb and fluoresce to an equal extent in the ultra-violet. In both cases, the ultra-violet absorption band concerned is separate and distinct from the visible absorption band which gives the substance its colour in alkaline solution. Accordingly, in both molecules we must have two different chromophore units, the one responsible for the ultra-violet absorption, the other for the visible absorption, and apparently the pyrone ring functions as a " fluorophore " only so far as the visible chromophore unit is concerned. The ultra-violet chromophore unit in both molecules is probably one of the benzene rings, but it appears certain that a phenyl radicle is not the visible chromophore in either phenolpthalein or fluorescein. This follows from the fact that neither substance shows any colour (visible absorption) in neutral or acid solution, but only in alkaline solution. Colour is in fact a characteristic only of the alkali salts of these compounds, and correspondingly it is only the alkali salts of fluorescein which fluoresce in the visible. The explanation of this difference is that in forming the salt from the neutral substance, a tautomeric change occurs which leaves the salt molecule with a quinonoid structure which the neutral molecule lacks. The generally accepted structural formulæ of neutral fluorescein and phenolphthalein and of their sodium salts are shown on p. 310.

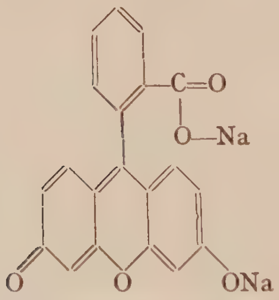
Granted that the visible absorption of both fluorescein and phenolphthalein in alkaline solution is connected with the quinonoid linkage in the salt molecule, we have still to explain the function of the bridge oxygen in promoting the visible fluorescence in the former case. The most reasonable view (originally proposed by Stark) appears to be that the closing of the middle ring by this bridge oxygen gives to the resultant molecule, when excited by absorption in the quinonoid chromophore, a greatly enhanced stability towards collisions with solvent molecules. In terms of this hypothesis, the sodium salt of phenolphthalein is still credited with the intrinsic capacity to re-emit the visible radiation which it absorbs, and it should therefore fluoresce under environmental conditions which reduce the possibility of de-activation of the photoexcited molecule by collisions with solvent molecules. Such conditions are apparently realised by dissolving the coloured salt in a solid (vitreous) medium such as gelatine, sucrose, succinic acid, benzoic acid, or benzamide, the solid solution when illuminated with visible light being now capable of giving a strong visible fluorescence. Numerous other organic dyestuffs such as malachite green, purpurin, methyl violet, and methyl blue which, though coloured, are like alkaline phenolphthalein incapable of fluorescing in ordinary liquid solvents, also fluoresce when dissolved in these vitreous solvent media.



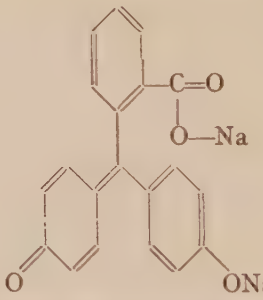
Fluorescein (neutral).



Phenolphthalein (neutral).



Sodium fluorescein (uranine).



Sodium salt of phenolphthalein.

Influence of Solvent Medium and Concentration on Fluorescence Capacity.—In discussing the effect of the solvent medium on the fluorescence capacity of a dissolved solute, due regard must of course be paid to any concomitant influence of the solvent on the absorption capacity of the solute. When a very marked alteration in the nature of the absorption spectrum is brought about by changing the solvent, we may be certain that chemical action is involved. For example, the fluoranes all give colourless solutions in alcohol but brightly coloured solutions in concentrated sulphuric acid, and it is only the latter solutions which give a visible fluorescence. The visible chromophore unit here formed is probably an addition complex of the fluorane and sulphuric acid. Chemical explanations are similarly required to account for the colour changes suffered by fluorescein, eosin, and phenolphthalein in passing from neutral or acid solvent media to alkaline solvent media.

Changing from one chemically indifferent solvent to another, the nature of the absorption spectrum of the solute is usually affected only to the extent that the spectral position of the absorption band or bands suffers a small displacement and the distribution of intensity within the band or band system simultaneously alters slightly. These effects can be referred to the influences of environment upon the constraints within the solute molecule—the same sort of influences which cause the displacement of absorption bands in passing from the vapour to the liquid or solid state. As is to be expected, similar differences are encountered in the fluorescence spectra of the solute in different solvent media. These differences are, however, of small importance compared with those which may exist between the yields of fluorescence obtained with different solvents. For purposes of comparison it is, of course, necessary to refer the yield of fluorescence always to the same amount of radiant energy absorbed. The ratio K of energy emitted to energy absorbed is called the specific capacity of fluorescence of the system. The dependence of K upon the nature of the solvent medium is most striking in the case of the dyestuffs such as malachite green and purpurin which absorb equally well in liquid and in solid media but are only capable of fluorescence when dissolved in highly viscous or solid solvents. For the more readily fluorescent dyestuffs, however, K also depends to some extent upon the solvent, and moreover the solvent which is most effective in promoting the fluorescence of one dyestuff is not always the best medium for another. Thus the specific capacity for fluorescence of fluorescein and of eosin (alkaline salts) is greater in alcoholic than in aqueous solution, whereas the reverse is true for æsculin. Again, the addition of neutral salts to an alcoholic or aqueous solution of a dyestuff usually has a marked weakening effect upon the fluorescence, although the absorption is not sensibly altered. On the other hand, the fluorescent yield is increased by the addition of such substances as gelatine, glycerine, or sugar which increase the viscosity of the solvent medium.

Unfortunately, most observations on solvent effect are robbed of a good part of their apparent significance by the fact that K is usually much more dependent upon the concentration of the fluorescing substance itself than upon the nature of the solvent medium. We have already noted for the case of benzene—and the same is more or less true for all its derivatives—that the capacity of the pure liquid to fluoresce is insignificant compared with that of a dilute solution of benzene in alcohol (or water, or ether, or pentane, etc.). The photoexcited benzene molecule appears to be very much less stable towards collisions with other benzene molecules than towards collisions with molecules of the solvent. Similarly, with large concentrations of a dyestuff such as fluorescein in liquid solution, no fluorescent emission is obtained despite the very marked absorption. Fluorescence appears at lower concentrations, but the optimum yield of fluorescence is only obtained by very extensive dilution. Strictly speaking, then, the solvent effect of itself can only be evaluated by measurement of K (the ratio of emitted to absorbed energy) within the range of (low) concentrations of the solute where K is independent of the concentration. This has been done in a few cases by Wawilow (*Z. Physik*, **31,** 750, 1925), from whose results it appears that the limiting specific capacity of fluorescence K_0 of fluorescein has practically the same value (*circa* 0·7) in water, in methyl alcohol, and in glycerine. When we take into account the enormous number of collisions which the photoexcited molecule of fluorescein suffers in solution during its normal life period, a value of K_0 of this magnitude implies, of course, a most remarkable lack of sensitivity of the photoexcited molecule to collisions with solvent molecules.

Wawilow has also carried out a detailed examination of the dependence of K upon the concentration of the dyestuff for different dyestuffs in different solvent media. In all the cases investigated, he finds that K for very dilute solutions remains independent of concentration over a small range, but then falls off exponentially with further increase in the concentration of the dyestuff. Fig. 42 illustrates the variation of K/K_0 with c (concentration of dyestuff in grams per litre) for the case of fluorescein (ammonium salt) in methyl alcohol. Above the limiting concentration c_0, K and c are connected by an equation of the type

$$K = K_0 e^{-\alpha(c-c_0)},$$

where α is a constant which is characteristic both of the solvent medium and also of the dyestuff considered. For fluorescein in two solvents such as water and glycerine for which the values of K_0 and c_0 happen to be almost identical, the ratio of the specific capacities of fluorescence of two solutions of the same concentration $c(c \gg c_0)$ is primarily governed by the ratio of the α's. The α for water is, from Wawilow's data, nearly four times that for glycerine, and it is for this reason that, of two solutions of fluorescein in water and in glycerine each containing say 9 grams of fluorescein per litre, the first fluoresces with only about one-tenth of the intensity of the second.

If the decay in the fluorescence capacity of the solute with increase in its concentration is to be ascribed to the occurrence of deactivating collisions (collisions of the second kind) between photoexcited and normal dyestuff molecules, it follows that the average life of the photoexcited molecule should also depend upon the concentration of the dyestuff in the same way as does the value of K. For true fluorescence, the average life of the photoexcited molecule is given by the period of decay τ of the luminescence. Within recent years, accurate methods of measuring periods of decay down to values of the order of 10^{-9} sec. have been evolved, and using such methods Gaviola (*Z. Physik*, **42**, 862, 1927) has shown that τ and K depend in exactly the same fashion upon the concentration, in agreement with the above expectations. It may be noted that for all dyestuffs in liquid solution for which the specific capacity of fluorescence is of the order of unity, τ is always found to have a value of about 5×10^{-9} sec. This is of the same order of magnitude as the undisturbed life of photoexcited atoms or molecules in gaseous systems.

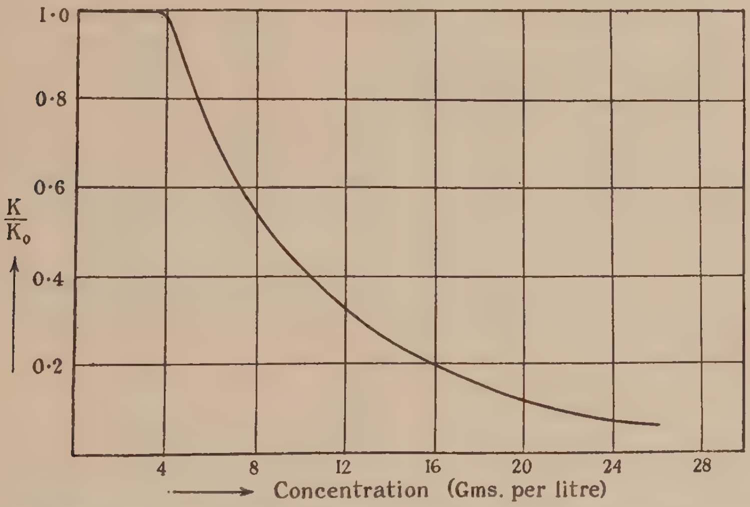


FIG. 42.—The specific capacity of fluorescence of fluorescein in methyl alcohol as a function of the concentration.

Other factors besides the concentration of the solute which should influence both K and τ are the viscosity of the solvent medium and the presence of foreign molecules. The influence of viscosity has been specially investigated by F. Perrin (*Compt. rend.*, **178**, 1978, 2252, 1924) who has shown that with increasing viscosity of the solvent medium but constant concentration of the solute dyestuff, the specific capacity of fluorescence of the system is increased. The reason for this is apparent if we interpret the increase of K to imply a smaller frequency of deactivation of the photoexcited dyestuff molecules by normal dyestuff molecules, since in the more viscous medium the velocity of diffusion of the solute molecules, which governs their collision frequency, is diminished.

Interesting observations of a qualitative nature by J. Perrin

(*Compt. rend.*, **184,** 1097, 1927) indicate that not only collisions between the photoexcited dye molecule A* and normal dye molecules of the same species, but also collisions between the photoexcited dye molecule A* and the molecules of another dye B, which absorbs in much the same spectral region as A, may be very effective in quenching fluorescence. The quenching action of B on the fluorescence of A is by Perrin called " resonance induction." Occasionally it is even more pronounced than the deactivating action of molecules of the type A on A*. Thus, the specific capacity for fluorescence of fluorescent blue is more markedly diminished by the addition of methylene blue than by increase in the concentration of the fluorescent blue itself. The effectiveness of the " resonance induction " appears to be greatest when the region of selective absorption of B coincides with the region of fluorescent emission of A. The fate of the transferred energy in such cases as these is probably degradation into heat motion, since no evidence of a sensitised fluorescent emission on the part of the added dyestuff B has yet been reported.

It has already been mentioned that the fluorescence of dyestuffs in liquid solution suffers appreciable diminution when neutral salts are added to the solvent medium. Observations by F. Perrin (*Compt. rend.*, **184,** 1121, 1927) and by West, Müller, and Jette (*Proc. Roy. Soc.*, **121**A, 294, 299, 313, 1928) indicate that the best explanation of this salt effect is to be found in deactivating collisions of the second kind between the photoexcited dye molecule and the *negative ion* of the added salt. Further, the order of the extinguishing powers of the ions is given as

$$\mathrm{I'} > \mathrm{CNS'} > \mathrm{Br'} > \mathrm{Cl'} > \mathrm{Ox''} > \mathrm{Ac'} > \mathrm{SO_4''} > \mathrm{NO_3'} > \mathrm{F'},$$

which is practically the order of their deformability, that is, of the ease of displacement of an electron in the peripheral shell of the ion. F. Perrin finds that easily oxidisable organic substances are also very efficient in quenching the luminescence of dyestuffs. Such substances which readily deactivate the photoexcited dyestuff molecule but possess no absorption band near that of the dye are called " anti-oxygens " by Perrin.

In very viscous or solid solvent media the photoexcited molecule should naturally be protected from many of the disturbing influences which operate in fluid media, and in particular from the deactivating action of the other solute molecules by collision. Accordingly, the effect of increasing the concentration of dyestuff upon its specific capacity of fluorescence should be considerably less than in liquid solution. The available evidence in this connection is contradictory. F. Perrin finds that solid solutions of eosin in glucose still show a strong fluorescence at concentrations for which, in liquid solution, the fluorescence would be almost completely extinguished. On the other hand, Lewschin (*Z. Physik*, **43,** 230, 1927) has found that for solid solutions of rhodulin or fluorescein in sucrose the value of K is at each concentration practically the same as in liquid solution. From this result Lewschin concludes that the mechanism of the quenching of the fluorescence must be the same in solid as in liquid solution, and since in the former case collisional deactivation of the photoexcited molecules by other solute molecules is excluded, our previous explanation of the quenching of fluorescence in liquid solution by such deactivating collisions is thus rendered questionable. The alternative explanation which is favoured by Lewschin is that within the concentration range where K varies with c there must be a considerable amount of polymerisation of the dyestuff in solution. The complex is still assumed to be capable of absorbing radiation within the visible absorption band, but apparently finds means of disposing of the absorbed radiation other than by re-emission. Effectively, then, all the absorbed radiation is not acquired by single dye molecules capable of re-emitting it as fluorescence. In support of this thesis it is known that, although the shape of the fluorescence spectrum of a dyestuff in solution does not alter appreciably with changing concentration, the shape of the absorption spectrum of many dyestuffs does alter very considerably with concentration, and, indeed, within that range of concentrations wherein K depends most upon c. Further evidence in support of complex formation in concentrated solution is obtained from the fact that the value of K for any concentration of the dyestuff within the quenching range increases with increasing temperature. This result can readily be explained on the basis of dissociation of the molecular complexes with elevation of the temperature, with consequent increase in the proportion of single molecules which can re-emit the radiation which they absorb. On the other hand, the view of deactivation by collision would appear to require that K should decrease with increasing temperature, consequent upon the increased frequency of collisions. Despite these facts, Lewschin's theory of complex formation does not appear to be supported by observation in one important particular. So far as accuracy of measurements permit, all wavelengths within the visible absorption band of a dyestuff are found to be equally effective in promoting fluorescence. This is a result which would certainly not be expected if the whole absorption band were composite of a band due to single molecules which could re-emit the radiation absorbed and a band due to complex molecules which could not re-emit. Much further work obviously requires to be carried out before a definite decision can be reached regarding the exact mechanism of the quenching of the fluorescence of dyestuffs in solution.

Photochemical Theory of Fluorescence of Dyestuffs in Solution.—In conclusion, brief mention may be made of a special theory of the origin of the fluorescence of complex organic substances in solution which aroused some controversy in the first part of the present decade. This theory, originally proposed by Perrin (*Ann. Physique*, **10,** 133, 1919), assumed that the fluorescence of these substances does not derive from re-emission of the absorbed radiation by the primarily excited molecule A, but from the emission of its excess energy by a nascent molecule B, the product of a photochemical transformation suffered by A. Examples of such "photo-chemiluminescence" in the case of gaseous systems are found in the excitation of the Balmer lines of the hydrogen atom by illumination of molecular hydrogen with light of the Schumann region (cf. p. 266), and of the alkali metal atom lines by illumination of the corresponding halide vapours with short wave radiation (cf. p. 227). For dyestuffs in solution, the fact that the fluorescent emission differs in spectral position from the absorption is formally not in disagreement with a photochemical mechanism for the origin of the luminescence, since the absorption should be characteristic of A, the emission of B. Other *prima facie* evidence is found in the circumstance that many dyestuffs in liquid or gelatine solution are bleached by the action of the light which induces them to fluoresce; concurrently with the bleaching, the fluorescence capacity of the system is destroyed. This of itself is not, however, sufficient justification for the conclusion that the photoluminescence in such cases is essentially different from true resonance or fluorescence on the part of the primarily excited molecule. On the contrary, there very seldom exists that intimate correlation of fluorescence and photochemical action which Perrin's theory demands. The results of several investigations in this connection by different workers * are briefly as follows :—

(*a*) Many fluorescent dye solutions can be exposed to bright sunlight for indefinitely long intervals of time, during which they absorb and re-emit an enormous quantity of radiant energy, without suffering appreciable photochemical action and without sensible diminution in their capacity for fluorescence.

(*b*) For dyestuffs which under special conditions undergo photochemical change with simultaneous destruction of their fluorescence, the velocity of the chemical change in different solvents does not run parallel with the brightness of the fluorescence.

(*c*) The temperature coefficients of the fluorescence process and the bleaching process are in general quite different. By cooling the illuminated system to −180° C., the photochemical action can be completely suppressed, while the intensity of fluorescence is not markedly affected.

(*d*) Depending upon the conditions, quite different photochemical processes can be induced without the nature of the fluorescent emission being affected.

(*e*) The photochemical yield for the same amount of radiant energy supplied depends upon the light intensity; the fluorescent yield is independent of the intensity.

From these and similar results it is now generally accepted that in the fluorescence of the dyestuffs in solution and in their photochemical destruction we are dealing with two entirely independent phenomena, corresponding to two alternative fates of the photoexcited molecule, viz. deactivation by fluorescent emission and disappearance by chemical action. Very high light intensities and (or) the presence of oxygen or some oxidising agent appear to be necessary for the photochemical destruction of the dye in solution. The nature of the chemical changes involved is further discussed in Chapter VII.

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* Wood (*Phil. Mag.*, **43**, 757, 1922); Pringsheim (*Z. Physik*, **10**, 176, 1922); Weigert (*ibid.*, **10**, 349, 1922); McLennan and Cabe (*Proc. Roy. Soc.*, **102A**, 256, 1923).

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CHAPTER VI.

CHEMILUMINESCENCE.

In the preceding Chapters certain photo-processes of a purely physical nature have been discussed in the light of modern quantum principles. The concept of definite stationary energy levels or states of activation of atoms and molecules has been found particularly useful in interpreting the various phenomena associated with the interaction of radiation and matter. When an atom or molecule originally in the state Z' is brought into a state of activation Z'' by absorption of radiation, the subsequent fate of the activated unit and of the excess energy which it contains depends to a great extent upon environmental conditions. The following possibilities have already been discussed in more or less detail :—

(1) Undisturbed re-emission of a part or the whole of the absorbed energy ($E'' - E'$) as radiation (*resonance spectrum*). The frequency emitted will be the same as that absorbed if the atom or molecule simply reverts to its original state Z', but it may be a different frequency if there are other energy levels to which the excited system can spontaneously pass with emission.

(2) Re-emission processes of a more complex nature owing to the disturbing influences of neighbouring molecules on the state of activation originally produced (*fluorescence*).

(3) Transfer of energy by collision from the active unit to an atom or molecule which is thus activated and subsequently emits its own characteristic radiation (*sensitised fluorescence*).

(4) Conversion by collision of the energy of activation into potential energy of a metastable (non-radiating) state, into kinetic energy of translatory motion, or into energy of excitation of other internal degrees of freedom of the system. In the absence of any emission, the energy originally absorbed is finally degraded to *energy of unordered heat motion*.

(5) *Ionisation*, followed by recapture of an electron and emission of one or more lines of the emission spectrum of the system.

Finally, the act of activation by absorption of radiation may precede a more or less complex chemical change—a photochemical process is the net result. The possibility of light emission or ionisation accompanying the photochemical change is not excluded.

When activation is brought about by means other than absorption of radiation, the same possibilities as regards the subsequent behaviour of the active unit are to be anticipated. Of special interest to the chemist is the case where activation results from the unordered heat motion of the molecules of the system, and chemical changes occur. Then we have the case of ordinary thermal chemical reactions. Another possibility of particular interest is the production of activated molecules *as a result* of normal chemical reaction, and the conversion of the energy of activation of the reaction products into radiant energy. Then we have the occurrence of *chemiluminescence*—the emission of radiation from a system in consequence of some chemical change which the system undergoes. Chemiluminescence is obviously the reverse phenomenon to photochemical change. In the latter we have two distinct methods whereby the absorbed radiant energy may be utilised in producing detectable chemical changes in the system. In a direct photochemical reaction, the molecule which absorbs the radiation plays a stoichiometric part in the reaction. In a sensitised photochemical process, the absorbing molecule is not a stoichiometric reactant, and, at least in one type of sensitised photochemical reaction, the function of the sensitiser is simply to transfer by collision the absorbed energy to another molecule which is thus made capable of reaction (cf. sensitised fluorescence). We have the counterparts of direct and sensitised photochemical processes in the two possible types of chemiluminescence where (*a*) the emitting unit is an activated product of the chemical change, (*b*) the emitting unit is not a reaction product but another molecule which obtains the energy necessary for its pre-activation by collision with activated reaction products.

As a preliminary to the study of photochemical change itself, it will be instructive to consider this inverse phenomenon of chemiluminescence, especially in respect of its interpretation along modern physical lines.

Detection of Chemiluminescence.—All reacting systems which give a visible luminescence are not necessarily emitting a *chemiluminescence*, since the energy liberated in a highly exothermic chemical process may be sufficient to raise the temperature of the system to that of incandescence. We must first enquire how we are to test for the presence or absence of true chemiluminescence in a system undergoing chemical change. Any system which is radiating energy in the absence of pre-illumination, mechanical or electrical influences (we thus preclude the occurrence of photoluminescence, triboluminescence, and electroluminescence) presents two possibilities (Trautz, *Z. physikal. Chem.*, **53,** 1, 1905; *Jahrb. Radioaktiv.*, **4,** 136, 1907) :—

(*a*) Independent of time the emission is always the same for a constantly maintained temperature. The radiation depends only upon the surface conditions and upon the temperature. It is the purely temperature radiation of the system, and, if the latter be enclosed in a "hohlraum," the radiation in the enclosure will immediately assume the characteristics of black body radiation (see

Chapter II.). Chemical changes *may* be taking place continuously in such a system, but, if so, they must be such as to exactly balance one another, i.e., a condition of dynamical equilibrium prevails.

(*b*) Constancy of temperature is not sufficient to ensure a constant emission. In this case an unbalanced chemical change is taking place. The continuously changing emission may simply correspond to pure temperature emission of the continuously changing system, or, superimposed on this, there may be chemiluminescence. These alternatives may be tested by enclosing the system in a hohlraum at constant temperature and examining the radiation in the enclosure. If now in spite of the chemical change the condition of black body radiation always exists, chemiluminescence is absent. The chemical process results only in the liberation or absorption of heat, between which and the radiation of the enclosure a continuous equilibrium takes place *via* the changing thermal absorption and emission capacities of the system. If, on the other hand, black body radiation does *not* prevail in the hohlraum, we can imagine the radiation present composed of two parts, the one a pure temperature radiation (black body under our conditions) corresponding to the temperature of the enclosure, the other part being chemiluminescence, with a spectral distribution depending intimately on the nature of the system. Its absolute intensity will vary with the rate of the chemical change producing the luminescence.

We see then that the necessary and sufficient criterion of chemiluminescence (in the absence of pre-illumination, mechanical and electrical disturbing effects) is the emission, from a constant temperature enclosure containing the reacting system, of radiation which for some position in its spectrum is of greater intensity than black body radiation at the same temperature. In the absence of the enclosure, a chemiluminescent system will at any instant radiate the purely temperature radiation corresponding to its instanteous physical state (and which will at all points in the spectrum be less intense than black body radiation at the same temperature), *plus* its characteristic chemiluminescent radiation. However, the resultant of these two spectra might still at all points be less intense that full black body radiation at this temperature, so that examination of the radiation *in an enclosure* containing the system is necessary to prove the *absence* of luminescence. On the other hand, the observation (without enclosure) of an emission which is more intense in some spectral region than the corresponding black body emission at the same temperature is sufficient proof of the *presence* of chemiluminescence. Naturally, then, experimental demonstration of the absence of chemiluminescence is much more difficult than proof of its presence. Black body radiation at a temperature of less than 500° C. is invisible to the human eye. Hence the mere optical observation of an emission from the reacting system below this temperature is enough to indicate the presence of the phenomenon. Failure to observe a visible emission below or even above 500° C. is not sufficient to disprove its presence. Very few reactions which are not obviously luminescent have as yet been subjected to the rigid "hohlraum" test mentioned above.

Chemiluminescent Reactions.—The luminescence met with in the slow oxidation of phosphorus and in the oxidation and decay of various animal and vegetable tissues is familiar to all, but the phenomenon is not confined to these few isolated cases. Trautz (*loc cit.*) has collated and studied in a more or less qualitative manner a great variety of chemical reactions which give a visible luminescence at temperatures below 360° C., and of which the following groups may be taken as typical :—

(1) Oxidation by air, oxygen, or hydrogen peroxide in alkaline or alcoholic potassium hydroxide solution of a large number of higher alcohols, aldehydes, higher fatty acids, amides, polyphenols, benzene and its homologues ;

(2) Oxidation of paraffins, higher alcohols, aldehydes, salts of fatty acids, diphenylamine, anthracene, etc. by heating with anhydrous alkali in air ;

(3) Oxidation of sugars, camphor, etc. by heating in air ;

(4) Action of oxygen or halogens on the vapours of the alkali metals ;

(5) Hydration of calcium and barium oxides and of calcium chloride ;

(6) Neutralisation of alkaline oxides with concentrated hydrochloric, sulphuric, or nitric acid ;

(7) Action of halogen vapours on ammonia, acetylene, molten alkali hydroxides, molten stearic and palmitic acids and their salts, etc. ;

(8) The so-called cold flames. Ether vapour, preheated to 260° C. and led into air, gives a bluish low-temperature flame ; similarly with stearic acid at 280° C., oleic acid, olive oil, and paraffin wax at 310° C., and sulphur at 180° C. Again, if a mixture of carbon bisulphide and air impinges against a glass plate heated to about 230° C., luminous burning of the mixture takes place at this temperature ;

(9) The Wedekind reaction—the reaction between phenyl magnesium bromide or iodide and chloropicrin.

Besides the above cases, the following additional chemiluminescent reactions which will be encountered in the course of the Chapter may also be noted :—

(10) Action of the halogen vapours on mercury vapour ;

(11) Reactions between sodium vapour and the vapours of mercuric chloride, iodide, and cyanide, cadmium iodide, hydrogen chloride, and phosphorus trichloride ;

(12) Slow oxidation of phosphorus and phosphorus trioxide ;

(13) Destruction of active hydrogen and of active nitrogen ;

(14) Oxidation of unsaturated silicon compounds.

It is to be remarked that, while all the cases cited above give a *visible* chemiluminescence, there is no reason why we should artificially restrict the phenomenon to emission within the limits of the visible spectrum. Reactions accompanied by emission of infra-red radiation are almost inevitably more numerous than those occurring with visible luminescence. As yet, such cases have received no consideration on account of the difficulties connected with the detection of such emission. So also luminescence in the ultra-violet is possible, though probably of less frequent occurrence. We need here only cite the glow associated with the slow oxidation of phosphorus which, when dispersed, is found to consist of a continuous emission in the visible together with a number of narrow emission bands lying in the ultra-violet. Other examples will be dealt with in the text.

With a few notable exceptions, chemiluminescent processes have up till the present received purely qualitative treatment. In the majority of cases, the phenomenon has been identified simply by the appearance of a visible emission which could not be due to temperature radiation alone. The colour of the luminescence has been noted and sometimes analysed spectroscopically, but no serious attempt has been made to trace the seat of the luminescence or to investigate the energetics of the accompanying chemical processes.

The unresolved luminescence is usually red, yellow, or green in colour. The presence of visible luminescence of shorter wave-length is often masked by the fact that the luminescence, when resolved, exhibits a broad emission band with maximum towards the long wave side of the visible spectrum. Solid and liquid systems usually give broad continuous emission spectra; for reactions occurring in the gaseous state, however, lines and bands may also be obtained.

Conditions for the Appearance of Chemiluminescence.—A scrutiny of the above-tabulated examples of chemiluminescent processes reveals the fact that they are all rapid reactions and exothermic. Probably the absolute *rate of reaction* has no direct bearing on the presence or absence of luminescence, but, of course, rapidity of reaction will be intimately related to the intensity of emission, if there is any possibility of emission at all. We should certainly expect a rough proportionality between rate of reaction and intensity of luminescence, and, although sufficient experimental evidence is not yet available to test this point thoroughly, it is at least known that the brightness of the emission usually increases rapidly with increase in the temperature of the system.

Since only reactions which luminesce in the visible or in the ultraviolet have as yet received attention, we must be dealing with states of internal excitation of the emitting units of at least 36,000 calories. This is important in relation to the observation that all the known chemiluminescent processes are *exothermic* in character. However complex the actual chemical change may be, one stage at least must result in the production of molecules possessing energy far in excess of their normal amount. It is in the disposal of this large surplus of energy during the formation of ordinary molecules that the possibility of light emission lies. In respect of this exothermic criterion, we may note that the bulk of the luminescent reactions encountered both in organic and in inorganic chemistry are oxidation processes, and, of course, these are just the processes which we normally associate with large heat evolution. It by no means follows, however, that all strongly exothermic reactions are necessarily luminescent. A preliminary to light emission is the excitation of some unit in the system to a labile state of internal excitation, and this may not always be possible. It is not inevitable that, even for highly exothermic reactions, resultant molecules which are active in the sense of possessing high internal excitation should be formed. For example, in an exothermic process of the type $A + B \rightarrow C + D$, the energy momentarily associated with the resultants C and D may exist simply as energy of translatory motion, in which case, of course, neither C nor D emits radiation. The possibility of this translatory energy being effective (by inelastic collisions of the first kind) to excite other molecules to luminescence will be considered later. Again, in few cases will an internal state of excitation of a molecule resulting from chemical action be such that it can revert to a state of lower energy content by a simple act of emission. Usually the normal state will be attained by conversion of the internal energy into energy of heat motion by collision. It may happen, however, that the excited resultant molecule, although not itself capable of spontaneous emission, can by subsequent collision be converted into a state of lower or even somewhat higher energy content, from which it can then revert to its normal energy level by emission of radiation. Under these circumstances the spectrum of the chemiluminescence produced should contain lines or bands which are characteristic of the emission, resonance, or fluorescence spectrum of the resultant. This type of chemiluminescent reaction, however, appears to be of very infrequent occurrence; in fact, there is no example in which the emission can with certainty be attributed to an excited resultant molecule. Most cases hitherto investigated appear to be reactions in which the activated resultant, by an inelastic collision of the second kind, excites either a reactant atom or molecule or a foreign atom or molecule which then emits. Well-authenticated cases in which it is definitely a reactant molecule which is induced to luminescence are found in the thermal decomposition of ozone at 400° C. (Stuchtey, *Z. wiss. Phot.*, **19**, 161, 1920) and in the reactions of the halogens with alkali metal vapours. When any molecule (or atom), reactant or non-reactant, other than the excited resultant itself, is the emission centre, we might term the phenomenon *sensitised chemiluminescence*, by analogy with sensitised fluorescence and sensitised photochemical reaction. The first clear recognition of sensitised chemiluminescence in this sense appears to be due to Strutt (*Proc. Roy. Soc.*, **88**A, 547, 1913) who found that when "active" nitrogen (produced by an electric discharge in nitrogen at low pressure) reacts with metal vapours to form nitrides, the chemical reaction is accompanied by a line emission of the characteristic (resonance) radiation of the free metal atoms. Here it is evident that energy transfer by collision must have preceded the act of emission. Numerous other well-investigated examples of energy transfer from resultant to a reactant molecule or to a foreign molecule also present in the system are found in the reactions of alkali metal vapours with the halogens, which cases we now proceed to discuss in detail.

THE REACTIONS OF ALKALI METALS WITH HALOGENS AND WITH MERCURIC HALIDES.

The luminescence accompanying the interaction of metal vapours and halogens at comparatively low temperatures was first studied quantitatively by Haber and Zisch (*Z. Physik*, **9,** 302, 1922). When a stream of nitrogen is saturated with sodium vapour at a temperature of 350° C. or higher and is led into an atmosphere of chlorine, the region of reaction between the sodium and the chlorine is visible as a bright yellow cone 5 to 10 cm. long, starting from the point of introduction of the sodium vapour. The brightness of the luminescence increases progressively with the temperature of saturation of the nitrogen current. Provided this does not exceed 470° C. (vapour pressure of $Na = 2$ mm. Hg), the maximum temperature of the flame is calculated from thermochemical data to be less than 525° C. Under these conditions, the luminescence when resolved and photographed is found to consist of the sodium D doublet and a faint continuous background. This latter probably corresponds to the purely thermal radiation of the reacting system, which should be barely visible to the eye at 525° C. The intensity of the D lines, however, far exceeds what could possibly be attributed to temperature alone, and their occurrence in the flame spectrum must be intimately related to the chemical reaction occurring in the system.

The net result of the chemical reaction is the formation of NaCl molecules, but the process probably takes place in more than one stage (cf. p. 332). The sodium chloride molecules at the moment of their formation are rich in energy, but naturally are not themselves capable of emitting the D lines. This can only be done by neutral sodium atoms, and since ordinary temperature excitation of Na atoms at 525° C. cannot produce the observed intensity of the D line, we must conclude that the normal concentration of excited Na atoms is artifically increased through energy transfer from reaction products to Na atoms by collision.

Haber and Zisch find that the efficiency of luminescence is very small, in other words only a small fraction, of the order 10^{-4}, of the NaCl molecules which are formed actually excite Na atoms to resonance. Alternative modes of deactivation of the sodium chloride are presented by collision with N_2 (and Cl_2) molecules, and activated Na atoms may themselves be deactivated by encounter with the diluent N_2 molecules before they radiate their energy.* It is significant that Beutler, Bogdandy, and Polanyi (see below), working with very low partial pressures of sodium vapour and chlorine and dispensing with nitrogen as diluent, have obtained an intensity of luminescence amounting to 10 per cent. or more of the maximum theoretical value.

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* The latter effect is probably multiplied by repeated absorption and re-emission of the D lines within the reaction zone.

Haber and Zisch also tested the possibility of luminescence accompanying the reactions of sodium vapour with bromine and iodine vapours. Using the same method of investigation, the D line is again present in the reaction zone, but is of much feebler intensity than in the case of sodium and chlorine. These investigations have been extended recently by the work of Terenin and Lialikov and of Polanyi and co-workers. The first-named authors (*Naturwiss.*, **14,** 83, 1926) have made a spectroscopic investigation of the chemiluminescence associated with the reactions between alkali metal vapours and iodine vapour. For sodium, the D line (the first in the Principal Series) is observed, in confirmation of the result of Haber and Zisch. With potassium and with rubidium, the first *two* lines ($1S - 2P$ and $1S - 3P$) in the Principal Series of the emission spectrum of the alkali metal are observed in each case. Besides these lines, emission bands are also present, attached to the lines. These appear to be identical with the bands found in the fluorescence and absorption of alkali metal vapours, from which it is concluded that excited alkali metal molecules are also present in the system. On the other hand, they note the complete absence of any emission on the part of the other reactant—the iodine molecule.

Beutler and Polanyi (*Naturwiss.*, **13,** 711, 1925), dispensing with nitrogen as carrier of the sodium vapour stream and using low concentrations of reactants (partial pressures up to about 0·1 mm.), found that besides the halogens a large number of inorganic compounds—HCl, $HgCl_2$, HgI_2, CdI_2, PCl_3, and $Hg(CN)_2$—react with sodium vapour at comparatively low temperatures with emission of the D line. No luminescence was observed, however, with tellurium chloride or iodide, with aluminium chloride, or with organic halogen compounds. A more complete spectroscopic analysis of the luminescence accompanying several of the above reactions revealed the fact (Beutler, Bogdandy, and Polanyi, *Naturwiss.*, **14,** 164, 1926) that besides the D line many other lines of the Principal, 1st and 2nd Subordinate Series, and also the line $1S - 3D$ occur in the emission, although with much feebler intensity. The accompanying table gives the various emission lines, with intensities relative to the D line, for the reactions of sodium vapour with $HgCl_2$, Cl_2, Br_2, and I_2. A cross denotes that the line referred to is present, but is very weak.

Under E is given the energy (in kilo-calories) required to excite the sodium atom from its normal state ($1S$) to the upper quantum level corresponding to the emission referred to. For the reaction between potassium and mercuric chloride vapours, various emission lines of the potassium arc spectrum: $1S - 2P$ up to $1S - 5P$, $2P - 3S$ up to $2P - 5S$, $2P - 5D$ up to $2P - 8D$ and $1S - 3D$ are observed. For the reaction of sodium with mercuric chloride, the mercury resonance line 2537 Å also appears, although with only

TABLE XXXV.

Line.	λ(μμ).	E (Kilo-cal.).	Intensity of Excitation.			
			$HgCl_2$.	Cl_2.	Br_2.	I_2.
$1S-2P$	589·0	48·3	100	100	100	+
$1S-3P$	330·3	86	1·5	0·05	0·015	
$1S-4P$	285·3	99·7	0·05	+		
$1S-5P$	268·0	106	0·005			
$1S-6P$	259·4	109·6	0·0005			
$2P-3S$	616	94·5	+	+	+	
$2P-4S$	515	103·3	0·15	+		
$2P-5S$	475	108·0	0·2	+		
$2P-6S$	454	110·5	0·05	+		
$2P-7S$	442	112·3	0·02	+		
$2P-8S$	434	113·5	0·02	+		
$2P-4D$	568	98·2	1	0·5	0·15	
$2P-5D$	496	105·1	0·3	+		
$2P-6D$	467	108·9	0·3	+		
$2P-7D$	450	111·2	0·1	+		
$2P-8D$	439	112·7	0·05	+		
$1S-3D$	346	82·6	0·005	0·005		

about one-hundredth the intensity of the D line. The mercury lines 3663 and 3131 Å are also faintly observed. Finally, in all cases of luminescence with sodium, various band spectra of low intensity appear. One of these, which occurs in all the reactions, agrees in position (571-658 $\mu\mu$) with a band emission obtained by Wood for the excitation of sodium vapour with slow cathode rays.

Contrary to the case of the sodium—mercuric chloride reaction, Haber and Zisch failed to detect an emission of the mercury resonance line in the reaction between mercury vapour and chlorine. The *band* luminescence observed in this and other mercury-halogen flames will be discussed later. On the other hand, Fränz and Kallmann (*Z. Physik*, **34,** 924, 1925) have found that if mercury vapour is added to a stream of nitrogen already charged with sodium vapour before this is led into chlorine, the spectrum of the yellow reaction zone contains not only the sodium line but also the Hg line 2537 Å. The intensity of the latter is somewhat smaller than, but apparently of the same order of magnitude as, that of the D line. Absence of sodium vapour cuts out both lines. It is clear then that the source of the excitation of the mercury line is to be sought in the reaction between the sodium and chlorine. We have here one of the best examples of sensitised chemiluminescence. When bromine is substituted for chlorine, the D line is still observed in the luminescence, but not the mercury resonance line. Apparently, then, the reaction products in the sodium-bromine reaction are not capable of exciting mercury atoms to resonance by energy transfer.

An appreciation of the above experimental phenomena requires an examination of the energetics of the individual chemical processes concerned and of the various possibilities of energy transfer by collision. These were first discussed in detail by Fränz and Kallmann (*loc. cit.*) with special application to the reactions of the halogens with sodium and with mercury. We will deal first with the possibilities of energy transfer from reaction product to emission centre.

Excitation by Energy Transfer.—The excess of energy contained in a nascent reaction product AB* may be present in two forms, (*a*) as internal energy of excitation, (*b*) as kinetic energy of translatory motion. Further, the chemical elementary process or reaction stage from which results this nascent product may be either an addition or a substitution reaction, of which we may take as typical

$$(\alpha)\ A + B \rightarrow AB^* \text{ and } (\beta)\ A + BC \rightarrow AB^* + C$$

respectively. We will assume that the kinetic energy of translatory motion of the reactants before collision is small in value compared with the chemical energy liberated.

For an addition reaction of the type (α), it is then impossible that any appreciable fraction of the energy associated with product AB* should be energy of translatory motion. The law of conservation of linear momentum requires that the net momentum of the system (A, B) should be the same before and after the binary collision, in other words, the translatory motion of AB* is completely determined by the relative velocity of A and B before collision, and not by the chemical energy which is liberated as a result of the combination. The latter energy must be held by AB* as internal energy of excitation.

On the other hand, for a substitution reaction (β), the condition of conservation of momentum does not fix the absolute velocities of the resultants. The energy of reaction may now appear either as internal energy of one or both products, or as kinetic energy of translatory motion of the products (these separating with a large relative velocity), or partly as internal and partly as kinetic energy. If the latter be represented by E, it will be shared between the products of mass m_1 and m_2 in the proportions

$$E_1 = \frac{m_2}{m_1 + m_2} \cdot E; \qquad E_2 = \frac{m_1}{m_1 + m_2} \cdot E \qquad . \quad (1)$$

Again, the molecule AB will usually possess many possible states of internal excitation (vibration and rotation) corresponding to lower energy levels than the highest which *could* be attained by use of the whole energy of reaction. It is improbable therefore that the product AB of a substitution reaction will retain as internal energy the whole or nearly the whole of the available energy. We see then that as regards the subsequent excitation by collision of a molecule D, which requires an energy not much less than the energy of reaction, the probability is smaller for a substitution than for an addition reaction.

Internal energy of a reaction product AB* may be used up to the whole amount for purposes of internal activation of D by collision (collision of the second kind). Any excess over and above what is required by D may be retained wholly or in part by AB as internal energy (corresponding to a lower internal energy level) or it will appear as kinetic energy of translatory motion of AB and D after impact. This kinetic energy will be divided between the molecules in inverse ratio to their masses in accordance with (1) above.

The whole of the *kinetic energy* of a reaction product AB is *not* available for internal excitation of another molecule D by collision (collision of the first kind). No particle can give up its translatory energy completely to activate another particle. This follows from the fact that the total linear momentum of the rapidly moving molecule AB and the (comparatively) stationary collision partner D must remain unaffected by the collision, so that part at least of the translatory energy must remain as such. If a rapidly moving molecule of mass m_1 and with kinetic energy E_1 collides with a stationary mass m_3, then, under the most favourable condition that after collision the two masses travel together, there still remains as kinetic energy an amount

$$E' = \frac{m_1}{m_1 + m_3} \cdot E_1$$

and only the energy

$$E_1 - E' = \frac{m_3}{m_1 + m_3} \cdot E_1 \qquad . \quad . \quad . \quad (2)$$

is available for activation of the molecule D. It follows from (2) that the conditions are most favourable for an activation when the mass m_1 is small compared with m_3. Only for collisions of a high-speed electron with an atom, or of a very light atom with a very heavy one, is practically the whole kinetic energy available for activation.

If the reaction product AB* of either (α) or (β) first suffers collision with an indifferent molecule Z, the whole or part of the internal energy AB* may be converted into kinetic energy of AB and Z. The probability of subsequent excitation of D by collision with either AB or Z is small, not only because of the smaller amount of energy available, but also on account of the above fact that a molecule cannot give up the whole of its translatory energy to activate another molecule.

It must be borne in mind that the conclusions drawn above refer only to the *possibilities* of energy transfer by collision from a reaction product to an atom or molecule capable of excitation—possibilities as limited by the laws of conservation of energy and linear momentum. The behaviour of two colliding molecules or atoms is, however, determined by other dynamical factors besides these—factors which the complexity of the actual atoms and molecules does not yet permit us to take into account, so that we can say very little regarding the actual *probabilities* of any of these possible energy exchanges.

Ternary Collisions in Addition Reactions.—In the above we have tacitly assumed that reactions of both types (α) and (β) actually do occur by simple binary collisions between the reactants. The truth of this assumption for the case of addition reactions has been questioned by Born and Franck (*Z. Physik*, **31,** 411, 1925). Let us suppose for simplicity that pre-activation of the reactants is not necessary and that steric factors are also absent. The total energy contained in the system immediately after reaction must then be equal to the sum of the kinetic energies of the reactants and the chemical energy released. This gross amount of energy may have any value corresponding to the infinitely variable value of the first term. The question now is, can this energy be disposed of by the resultant or resultants of the reaction with simultaneous conservation of energy and of linear momentum. This is always possible when there are two resultant molecules. The total available energy may be shared between these as internal energy and kinetic energy of translatory motion. The internal energy can in general only have certain discrete values determined by quantum conditions, but the kinetic energy is not quantised and can have any value. The reaction products can therefore always separate with *relative* velocities such that conservation of momentum is maintained and *absolute* velocities such that conservation of energy is also maintained. For an addition reaction, however, where there is only one resultant molecule, the linear momentum and therefore the kinetic energy of this resultant is uniquely determined by the arbitrary original momentum of the reactants. If then the net energy (kinetic energy of resultant *plus* chemical energy released *minus* kinetic energies of reactants) does not exactly correspond in value to one or other of the possible internal energy levels of the resultant, the reactants will not in general combine to form a stable molecule but will separate again after the collision. The probability of the above condition being fulfilled is very remote, since the internal energy levels of a molecule are sharply defined by quantum conditions. The chance of an addition reaction taking place by a *binary* collision will, therefore, be very small unless the resultant *at the instant of its formation* can lose the surplus energy over and above that required as internal *plus* kinetic energy by emission of radiation. Confining ourselves to the case of binary collisions between atoms, it appears necessary, in the light of Franck and co-workers' observations on the possibility of optical dissociation of various types of diatomic molecules, to differentiate between the addition reactions such as $Cl + Cl \rightarrow Cl_2$ which yield a homopolar product and reactions such as $Na + Cl \rightarrow NaCl$ which have an ionic dipole as resultant. Since it is impossible to dissociate the homopolar Cl_2 molecule into *normal* Cl atoms in an elementary act of absorption, we must conclude that any complex which may momentarily be formed by collision of two normal Cl atoms does not represent a labile excited state of the Cl_2 molecule and therefore cannot become such a molecule by any spontaneous process of emission. In order that association by collision of Cl atoms to form a Cl_2 (normal or excited) molecule may occur, it is necessary that the collision should involve a third atom or molecule (*ternary* collision), whose function it is to serve as an energy sink or reservoir for the disposal of the surplus energy which cannot be got rid of by radiation. On the other hand, the ionic molecule NaCl *can* be dissociated into two normal atoms by absorption of radiation, and the reverse process must also be possible. The reversal can be regarded as the association of a normal Na and a normal Cl atom by binary collision to form a momentary (Na — Cl) complex, which really represents a labile form of the normal Na^+Cl^- molecule and which can in fact assume the ionic configuration by emission. From this it appears that the addition reaction $Na + Cl \rightarrow NaCl$ must be possible of occurrence without the intervention of ternary collisions. A closer examination suggests, however, that the efficiency of molecule formation by binary collision even in this case may be very small. For complete association to occur, the non-ionic complex Na—Cl must within the period of its existence as a collision complex pass spontaneously by emission to the ionic configuration. The average life of the complex, regarded as a labile state of the normal NaCl molecule, cannot however be much less than 10^{-8} sec., whereas its average life, regarded as a collision complex, is only about $10^{-12} - 10^{-13}$ sec. If the spontaneous transition does not happen within the latter time interval, the Na and Cl atoms separate again and the opportunity for association is lost. It follows that in spite of the difference between such addition reactions as $Cl + Cl \rightarrow Cl_2$ and $Na + Cl \rightarrow NaCl$ in respect of intrinsic possibility of occurrence, their actual probabilities of occurrence under ordinary circumstances are almost equally remote.

The above considerations apply only to reactions taking place in the gaseous phase. Association of atoms to molecules can readily take place on surfaces, since the surface can obviously function as the third molecule in the ternary collision otherwise necessary. If the third partner in a ternary collision is a molecule D with an energy level of excitation less than the energy of reaction, the latter energy may be directly utilised in the ternary collision for the purpose of excitation of D, the surplus energy then appearing as kinetic energy of the resultant and of D, and (possibly) as internal energy of the resultant. It should be remembered, however, that ternary collisions necessarily occur much less frequently than binary collisions; with regard to the feasibility of a reaction mechanism involving ternary collisions, each case must be considered on its own merits.

Mechanism of the Reactions of Alkali Metals with Halogens and with Mercuric Halides.—In the gaseous state these reactions have been studied both in the presence and in the absence of a diluent gas (nitrogen). The latter case is the simpler from a theoretical standpoint and the mechanism of reaction will principally be discussed on the basis of experimental data obtained under such conditions. As already mentioned, when the only gases present are the reactants, a much greater chemiluminescent emission is observed than when nitrogen is added, and further, for sufficiently low partial pressures of reactants, ternary collisions need not be taken into account.

Although in these chemiluminescent processes neither the reaction mechanism nor the types of energy transfers may yet be regarded as settled, the recent work of Polanyi and his co-workers * marks an advance, since methods are developed which help towards the elucidation of the nature of these reactions and certainly lead to mechanisms supported by a variety of evidence.

Polanyi employs pressures of reacting gases ($Na + Cl_2$, $Na + I_2$, etc.) of the order of 10^{-2} to 10^{-3} mm. Under such conditions, " cold " flames are obtained which are of considerable length, owing to the fact that the mean free path of the molecules is several centimetres. The emission observed is a true chemiluminescence as, owing to the relativity small amounts of material transformed and the good thermal conductivity at such pressures, the flame temperature (usually about 300°) is kept well below that at which a visible emission is perceptible. Two types of " flame " were investigated ; in the one, the alkali metal vapour and the halogen streamed (in approximately equivalent proportions) into the heated reaction tube from opposite ends, while in the second, the halogen entered through a nozzle placed centrally in the tube containing the alkali metal vapour in excess. In either case, the method developed for the study of the reaction mechanism depends on measurements at various points along the reaction tube of (1) the intensity of emission and (2) the extent of reaction (i.e. amount of alkali salt formed). The correlation of such determinations suggests certain inferences in regard to the reaction mechanism, and combination with other data such as the partial pressures and velocities of the reacting gas molecules makes a quantitative treatment possible.

Without entering into details, the most important of Polanyi's results for the alkali metal—halogen reactions may be summarised as follows :—

(1) For opposed gas streams of the two reactants, the curve obtained by plotting NaCl precipitated against length of reaction tube (precipitation curve) is not symmetrical but falls more slowly on the side at which alkali metal enters. The maximum on the light emission curve does not coincide with the maximum on the precipitation curve, but is displaced several centimetres to the alkali metal side. (With nozzle flames, the light emission curve is much broader than the precipitation curve.)

(2) Increasing the temperature of the reaction zone causes a diminution in the intensity of the emission.

(3) Increasing the partial pressure of alkali metal vapour causes an increased " light-yield," the increase being more than proportional to the increase in p_{Na} (or p_K, etc.).

(4) For the reaction between Na and Cl_2, addition of hydrogen is accompanied by HCl formation.

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* Beutler and Polanyi (*Z. Physik*, **47**, 379, 1928 ; *Z. physikal. Chem.*, [B], **1**, 3, 1928) ; Bogdandy and Polanyi (*Z. physikal. Chem.*, [B], **1**, 21, 1928) ; Polanyi and Schay (*ibid.*, [B], **1**, 30, 1928).

These observations may be satisfactorily accounted for by the assumption of mechanisms of the type (M = alkali metal atom, X = halogen atom) :—

Primary process : (1) $M + X_2 \rightarrow MX + X$ (in gas phase),
Secondary processes : (2*a*) $M + X \rightarrow MX$ (on walls of reaction vessel),
(2*b*) $M_2 + X \rightarrow MX + M$ (in gas phase),

together with the assumption that the halide (MX) molecules formed in (2*b*) contain as internal energy of activation the major part of the heat of reaction, and transfer it to alkali metal atoms on collision, thereby stimulating the latter to emission. It will be noticed that, in agreement with the Born-Franck theory, the reaction $M + X \rightarrow MX$ is assumed—in the absence of ternary collisions—not to occur in the gaseous phase, and further that the reaction leading to the activated resultant whose excess energy is utilised for the excitation of the emitting alkali metal atom is (2*b*) and involves alkali metal molecules M_2 (Na_2, K_2, etc.).

Result (2) is important for the theory of reaction mechanism. For the $Na - Cl_2$ reaction, it is found that the diminution in the intensity of emission (D line) with increasing temperature is an exponential function of T. In terms of reaction (2*b*), this decrease is due to increasing dissociation of Na_2 molecules on raising the temperature, and from the observed falling off in emission it is possible to calculate the the heat of dissociation (D_{Na_2}) of Na_2 molecules. In this way the value $D_{Na_2} = 18 \pm 2$ kilo-cal. is obtained, which is not in serious disagreement with the value $D_{Na_2} = 23 \pm 3$ kilo-cal. obtained by Loomis (cf. p. 269) from optical measurements. Further, according to Polanyi, the fraction of sodium vapour present in the diatomic condition is sufficient to account for the experimentally observed emission. The assumption that the light-emitting process is in some way coupled with Na_2 (or K_2) molecules is also supported by observation (3), that increasing the partial pressure of alkali metal causes a sharp increase in the chemiluminescence. With opposed streams of reactants, it is found, for example, that in the $Na - Cl_2$ reaction only 1 in 1000, in the $Na - I_2$ reaction 1 in 2000 elementary processes leads to the emission of a quantum. The smallness of the " light-yield " is here due to the secondary reaction

(2*a*) $Na + Cl \rightarrow NaCl$ or $Na + I \rightarrow NaI$ (wall reaction)

occurring preferentially, and to the fact that activated molecules of NaCl resulting from reaction (2*b*) reach the wall without colliding with an Na atom. With " nozzle flames," however, when halogen is passed into excess sodium vapour, the light-yield increases many times, and by sufficiently increasing p_{Na} light-yields of 35 per cent. are obtainable in the $Na - Cl_2$ reaction.

Analysis of the experimental results on the basis of the mechanism given above leads to the following conclusions :—

(*A*) Reaction (1) takes place after every collision between sodium atoms and chlorine molecules; in fact, the observed rate is greater than the calculated, if one employs for the diameters of Na and Cl_2 the values given by kinetic theory.[†] This conclusion is in harmony with the modern view that in exothermic processes [‡] which are double decompositions and in which atoms are reactants, every collision is effective. (The reverse endothermic reactions thus require an energy of activation which is equal to the heat of reaction.)

(*B*) Reaction (2*b*) $Na_2 + Cl \rightarrow NaCl + Na$, also exothermic, occurs at every collision between the reactants; on the other hand, reaction between Na and Cl atoms to form NaCl *in the gas phase* would appear to take place under the conditions employed only in 1 in 10,000 collisions.

(*C*) The probability that upon collision of $NaCl^*$ molecules (formed in (2*b*)) with Na atoms (the process activating the Na to emit the D line) an emission of light follows is of the order of 0·7 to 1·0. For the $Na - Br_2$ and $Na - I_2$ reactions, the corresponding factor is less, but still appreciable. The " effective area of collision " between $NaCl^*$ and Na seems to be about twice the " kinetic-theory " value.

The above refers to reactions between alkali metals (Na or K) with the halogens (Cl_2, Br_2, or I_2) and also with ClCN and BrCN. Different behaviour is obtained, however, if in place of the halogens we substitute the vapour of $HgCl_2$ or $HgBr_2$ (also SO_2Cl_2), and a reaction mechanism of a different type must be presumed. The alkali metal—mercuric halide reactions exhibit the following characteristics:—

(1) For the " nozzle flame " reactions, the precipitation curve coincides with the luminescent emission curve.

(2) Increase of temperature of the reaction zone does not affect the light-yield.

(3) The light-yield increases with increasing partial pressure of alkali metal vapour, but not so markedly as in the reactions of alkali metals with halogens.

(4) For the $Na - HgCl_2$ reaction, no HCl is formed when hydrogen is present.

These observations can be adequately interpreted in terms of the reaction scheme (for the case of $Na + HgCl_2$):—

(1) $Na + HgCl_2 \rightarrow NaCl + HgCl$ (primary process)
(2) $Na + HgCl \rightarrow NaCl + Hg$ (secondary process),

both reactions occurring in the gas phase, and reaction (2) being the one that yields the NaCl molecule whose internal energy of excitation eventually leads to the observed chemiluminescence. According to this theory no halogen atoms are formed in the primary reaction, and the secondary process occurs as a double decomposition involving *atomic* sodium. The absence of a temperature effect on the luminescence is thus due to molecular sodium (Na_2) not being necessary for the secondary reaction; the fact that in the Na — $HgCl_2$ reaction HCl is not formed in the presence of hydrogen while it does result in the Na — Cl_2 reaction, the theory attributes to the absence in the one and the presence in the other of chlorine atoms. The increase of the light-yield with increasing p_{Na} is accounted for by the circumstance that more of the activated NaCl molecules formed in (2) collide with and transfer their excess energy to Na atoms before they reach the wall. The rate of increase of the intensity of emission with increasing p_{Na} is naturally less marked than in the Na — Cl_2 reaction, since in the latter, in addition to the effect just mentioned, increase in the partial pressure of sodium increases the concentration of Na_2 molecules, whose reactivity is the primary cause of the emission.

[†] According to Polanyi, one must assume that the sum of the radii of Na and Cl_2 effective for collisions is about $\sqrt{10}$ times greater than the " kinetic theory " value.

[‡] Each of the reactions $Na + Cl_2 \rightarrow NaCl + Cl$, $Na + Br_2 \rightarrow NaBr + Br$, and $Na + I_2 \rightarrow NaI + I$ is exothermic (for data, see p. 334).

Energetics of the Reactions of Alkali Metals with Halogens and Mercuric Halides.—For the reactions between sodium vapour and the halogens, Beutler and Polanyi (*Z. Physik*, **47**, 379, 1928) calculate the following heats of reaction :—

Reaction.	Heat Evolved (kilo-cal.).		
	X = Cl.	X = Br.	X = I.
(2*a*) .. (Na) + (X) → (NaX)	93·4	85·8	68·7
(1) .. (Na) + (X_2) → (NaX) + (X)	34·9	40·6	33·5
(2*b*) .. (Na_2) + (X) → (NaX) + (Na)	75·4	67·8	50·7

The round brackets indicate that all the substances are in the gaseous state, and the values of the heats of the reactions (Na_2) + (X) → (NaX) + Na are based on the estimate of 18 kilo-cal. for the heat of dissociation of diatomic sodium molecules.

In each of these reactions the D line constitutes the major part of the chemiluminescence, and it follows that the elementary process whose liberated energy is eventually utilised for the emission of this line must be—in kilo-calories per mole.—at least 48·3. From the data just given, it is seen that the reactions of type (1) are not the ones concerned. We are then left with processes (2*a*) and (2*b*)—in each of which sufficient energy is evolved—and also with processes (2*c*) $X + X \rightarrow X_2$, which must also occur to some extent. Under the conditions of very low pressures employed by Polanyi and his co-workers, however, we must assume that reactions (2*a*) and (2*c*) take place only on the walls of the reaction tube and do not contribute sensibly to the observed emission. We must thus regard process (2*b*) as the one whose liberated energy is employed in bringing about the luminescence. Now reaction (2*b*) could cause an activation of atomic sodium in two ways; either (α) the Na atom itself formed in the reaction appears in the activated state and then emits, or (β) the NaCl molecules formed retain—in the form of vibrational energy †—the greater part of the heat of reaction and transfer it on collision to Na atoms which have played no part in the reaction. Against assumption (α) there is certain spectroscopic evidence; furthermore, experiments carried out by Polanyi and Schay (*loc. cit.*) on the effect of added nitrogen upon the emission tell in favour of assumption (β). These investigators found that addition to the highly dilute reacting systems $Na + Cl_2$ and $Na + I_2$ of small quantities of nitrogen ($p_{N_2} < 10^{-1}$ mm.) causes a very marked decrease in the intensity of the emission. This can hardly be due to deactivation of Na* atoms by collisions of the second kind with nitrogen, since the pressure of N_2 required to reduce the resonance emission of sodium vapour to the half-value is 1·6 mm.‡ We must then attribute the major part of the action of N_2 to its deactivating NaCl* on collision and thus preventing collisions between NaCl* and Na.

The theory given appears satisfactorily to account for the strong emission of the D line when highly dilute gas mixtures are employed. It has been shown, however, that under such conditions other lines are emitted, though much less strongly, and the data given in Table XXXV. (p. 326) show that the emitting units must have received energies up to 113·5 kilo-cal. per mole. Since on our theory the maximum energy available for activation is only 75·4 kilo-cal.—the value in the case of the $Na - Cl_2$ reaction—it follows that transfers of energy to Na atoms other than by binary collisions with NaCl* molecules (formed in (2*b*)) must occur to some extent. The simplest explanation of the emission of these lines ($1S - 3P$, $2P - 4S$, etc.) of Na would seem to be that double activation of sodium atoms by collision with two NaCl* molecules (i.e. $Na + NaCl^* + NaCl^* \rightarrow Na^{**} + 2NaCl$) may take place. Evidence for double activations of this type has been obtained by Beutler and Josephy (*Z. physikal. Chem.*, **139,** 482, 1928) in the fluorescence as well as in the chemiluminescence of dilute gaseous systems. In this connection the $Na - HgCl_2$ reaction is of special interest. This takes place according to the scheme—

$$(1)\quad Na + HgCl_2 \rightarrow NaCl + HgCl + 24 \text{ kilo-cal.}$$
$$(2)\quad Na + HgCl \rightarrow NaCl + Hg + 57 \text{ kilo-cal.}$$

The maximum energy which can be associated with the NaCl* formed in (2) is thus 57 kilo-cal., and even if one assumes that the HgCl molecules enter into reaction (2) endowed with *all* the energy liberated in (1), the figure is only raised to 81 kilo-cal. Yet the Hg (2537 Å) line which appears in the chemiluminescence requires an activation of the emitting Hg atom of 112 kilo-cal. The difference between this value and 57 kilo-cal. (or 81) is much too large to be made up by the kinetic energy of the colliding molecules at 300° C., and we must consequently assume that two nascent NaCl molecules formed in reaction (2) yield their excess energy to a mercury atom. According to Beutler and Josephy, the fact that $2 \times 57 = 114$ kilo-cal. lies very near to the energy of activation of Hg (112 kilo-cal.) favours a high efficiency for the energy transfer concerned. It is further considered probable that the $NaCl^*$ molecule formed in (2) carries away practically all the energy of reaction, retaining it as vibrational energy until it collides with the wall or with another molecule. The same authors also calculate that the number of ternary collisions—$NaCl^* + NaCl^* + Hg$—obtaining in the system is sufficient to account for the observed intensity of emission of the 2537 Å line.

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† Cf. Hasche, Polanyi, and Vogt, *Z. Physik*, **41**, 583, 1927.

‡ The quenching action of nitrogen on the chemiluminescent emission by inelastic collisions between Na* atoms and N_2 molecules could be much greater than Mannkopff's value $p_{\frac{1}{2}}$ $(N_2) = 1·6$ mm. would suggest, if the observed chemiluminescent emission does not come direct from primarily excited Na* atoms but is transmitted from within the zone of reaction by multiple emission and absorption. That the nitrogen acts principally by deactivating NaCl* molecules is, however, suggested independently by the linear character of the plot of intensity of emission against the reciprocal of the pressure of added nitrogen (cf. Polanyi, *Z. physikal. Chem.*, [B], **1**, 384, 1928).

Other examples of multiple activation are encountered in the reaction between Na or K and Cl_2 when mercury vapour is present in the system. Beutler and Josephy found that with pressures of Hg vapour of 0·3 mm., the luminescent emission of $Na - Cl_2$ and $K - Cl_2$ flames contained the Hg lines given in Table XXXVI., which also gives the state of activation of the emitting Hg atom and the energy necessary to raise the normal atom to the state in question.

TABLE XXXVI.

Lines Emitted by Excited Hg Atoms in Reacting Mixtures of K (or Na) and Cl_2.

State of Activation of Hg.		2^3P_1.	2^3S_1.	2^1S_0.	3^3D.	3^3S_1.	4^3D.
Energy of activation (kilo-cal.)		112	176·5	181	202	202	218
Line emitted (Å)	$K+Cl_2$ reaction	(2537) ?	?	—	3663, 3655 3132, 3126 2967 ?	3341	3026, 3022 2654 ?
	$Na+Cl_2$ reaction	(2537) ?	4047 4358 5461	4078	3663 ?	—	—

The table shows that in the $K - Cl_2$ reaction, processes of activation supplying to Hg atoms 200-220 kilo-cal. must have occurred, in the $Na - Cl_2$ reaction, processes supplying 175-180 kilo-cal. From the theory given for the $Na - Cl_2$ reaction, the secondary reaction whose liberated energy is utilised for activational purposes is (2*b*) $Na_2 + Cl \rightarrow NaCl + Na$, and the maximum energy which may be associated with NaCl* resulting in this process is 75·4 kilo-cal. The process of double activation $NaCl^* + NaCl^* + Hg \rightarrow Hg^{**} + 2NaCl$ could thus supply only 151 kilo-cal., insufficient to account for the observed emission. If, however, we assume with Beutler and Josephy that the activating ternary collision is one of the type $NaCl^* + NaCl^* + Hg \rightarrow Hg^{**} + (NaCl)_2$, in which $(NaCl)_2$ is a double molecule and a first stage in the condensation to solid NaCl, an extra amount of energy of about 30 kilo-cal. is available for the purpose of activating the colliding mercury atom. We thus obtain 181 kilo-cal. as the energy which mercury atoms may receive from ternary collisions with two NaCl*'s, an amount sufficient to account for the observed emission. The energies corresponding to 151 and 181 kilo-cal. in the $Na - Cl_2$ reaction are for the $K - Cl_2$ reaction 167 and 195 kilo-cal. respectively, and are insufficient to explain the production of all the emitted Hg lines. To what processes of activation these can be attributed remains uncertain.

We have hitherto discussed the mechanisms of the reactions between Na and the halogens (and mercuric halides) for cases in which gaseous systems at low pressures were employed. When, however, a large excess of nitrogen is present, as in the experiments of Haber and Zisch and of Fränz and Kallmann, the mechanism of reaction may to some extent be different and other types of energy transfer may intervene. Thus for the $Na—Cl_2$ reaction, the secondary process

$$Na + Cl \rightarrow NaCl + 93{\cdot}4 \text{ kilo-cal.}$$

should now take place in the gaseous phase, ternary collisions ($Na + Cl + N_2$) promoting this type of change. Since the greater fraction of the sodium present is in the monatomic form, this secondary reaction should occur to an extent at least comparable with that of process (2*b*) $Na_2 + Cl \rightarrow NaCl + Na$. Now it is possible that nitrogen molecules after these ternary collisions, as well as nitrogen molecules which emerge from collisions of the second kind with NaCl* and Na*, are endowed not only with kinetic energy of translatory motion but also with internal energy of vibration. The assumption that internally activated nitrogen molecules are present in such systems has been made by Beutler and Josephy to account for the result of Fränz and Kallmann (cf. p. 326) that the 2537 Å mercury line is emitted by reacting systems containing Na, Cl_2, Hg, and N_2. It is suggested that the mercury atom receives the energy necessary for activation to the 2^3P_1 level by ternary collisions of the type $NaCl^* + N_2^* + Hg$, the combined vibrational energies of the colliding NaCl and N_2 molecules being utilised in the excitation of the Hg atom. According to this view, therefore, all the energy received by nitrogen molecules is not dissipated as thermal energy, but a portion is utilised for purposes of light emission.

Band Emission in the Reactions between Alkali Metals and Mercuric Halides and between Mercury and Halogens.—We have already noted the fact that in the reactions between alkali metals and iodine, a band emission attributable to diatomic alkali metal molecules is observed; the phenomenon is much more pronounced in the reactions under certain conditions between mercury halides and alkali metals and between halogens and mercury, in which cases, however, the bands emitted are due to a mercury halide molecule. Dealing first with the reactions between alkali metals and halides, these have been studied by Kondratjew (*Z. Physik*, **45,** 67, 1927; **48,** 310, 1928) and include the reactions of Na and K with $HgCl_2$, $HgBr_2$, HgI_2, $CdCl_2$, $CuCl_2$, and $CuBr_2$. These were investigated at low pressures (no N_2 present) at various temperatures between 130° and 370°. When the temperature of the reaction zone is sufficiently high, the chemiluminescence is exclusively composed of the lines of Na (or K) and derives entirely from the gaseous phase. With diminution of the temperature, however, considerable change in the character of the emitted light ensues. There appears a bluish-violet emission which comes from the walls of the reacting vessel, and the yellow D line emission of sodium is sensibly diminished. The lower the temperature of the reaction zone the more intense becomes the bluish-violet surface luminescence and the feebler the yellow line emission, and at a temperature of 130° C. the latter disappears completely. It has been shown that the blue glow is actually due to a surface reaction, the fall in intensity with increasing temperature being due to diminution in the amount of salt (or metal) adsorbed on to the walls. The spectrum of the bluish surface glow in the $K-HgCl_2$ reaction stretches from 560 to 310 $\mu\mu$, with maximum intensity at 410 $\mu\mu$. With increased dispersion, it exhibits a definite band structure, appearing as a great number of narrow bands running into each other, many of which coincide with the bands of the spectrum obtained by the passage of an electrical discharge through $HgCl_2$. Terenin (*Nature*, **117,** 843, 1926) has shown that the discharge spectrum derives not from $HgCl_2$ but from HgCl, and the same applies to the chemiluminescence under discussion. From the observed short wave-limit (310 $\mu\mu$) of the surface emission in the $K-HgCl_2$ reaction, we must thus presume that HgCl molecules are formed which are activated up to 92 kilo-cal. (per mole.). Now for the reaction in the *gaseous* phase (yielding the line emission of K), the most probable mechanism † is that represented by

$$\begin{aligned} K + HgCl_2 &\rightarrow KCl + HgCl \\ K + HgCl &\rightarrow KCl + Hg, \end{aligned}$$

whose heats of reaction, with all the substances in the gaseous state, are respectively of the order of 30 and 60 kilo-cal. A *strong* emission from the gaseous phase (i.e. an emission caused by an elementary, not a double, activation) of wave-lengths shorter than 480 $\mu\mu$ is thus not to be anticipated. If, however, the reactions take place on the surface so that the reactant mercury salt and resultant KCl are in the

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† Kondratjew (*loc. cit.*) prefers the scheme: $K + HgCl_2 \rightarrow KCl + Hg + Cl$; $K + Cl \rightarrow KCl^*$; $KCl^* + K \rightarrow KCl + K^*$.

solid state, it is possible to account for the observed emission. The heats of reactions

$$(K) + [HgCl_2] = [KCl] + (HgCl)$$

and

$$(K) + [HgCl\ ] = [KCl] + (Hg)\dagger$$

are now increased to about 70 and 100 kilo-cal. respectively, owing to the heat of sublimation of KCl being considerably greater than that of $HgCl_2$ (or HgCl). It should then be possible for HgCl molecules formed in the first of these reactions to be directly activated to about 70 kilo-cal., while the energy liberated in the second reaction, occurring on contiguous parts of the wall, might be utilised for the further activation of HgCl molecules. According to Kondratjew's calculations, the wall reaction forming HgCl is exothermic to the extent of 94 kilo-cal., and could of itself account for the observed emission.

For other reactions investigated by Kondratjew, a similar explanation of the band emission may be advanced. The spectral limits observed in these cases are :—

Reaction :	$K + HgBr_2$.	$K + HgI_2$.	$K + CdCl_2$.	$K + CuCl_2$.	$K + CuBr_2$.
Surface Emission	470-330 $\mu\mu$	560-360 $\mu\mu$	630-575 $\mu\mu$	550-390 $\mu\mu$	550-400 $\mu\mu$

In the last two of these reactions, the heats of the processes

$$[CuX_2] + (K) \rightarrow [KX] + (CuX)$$

appear to be sufficiently great to account for the short wave limit of the surface glow emitted.

Other reactions in which marked band emission is produced are the *mercury-halogen* reactions studied by Haber and Zisch and by Fränz and Kallmann. The low-temperature flames associated with these reactions differ markedly from those associated with the alkali metal-halogen reactions, not only as regards their nature but also in respect of the experimental conditions necessary for their production. Much greater partial pressures of the metal vapour (over 40 mm.) and considerable excess of halogen vapour are required to excite a visible luminescence, which contains no trace of line emission. Table XXXVII. summarises the main features of the emissions in these mercury-halogen reactions, the limits of the band spectrum being given both in wave-lengths and in terms of the corresponding energy changes (in kilo-cal). This energy change for any emission process fixes a *lower* limit to the energy content of the emitting centre at the moment of luminescence.

For the $Hg-Cl_2$ reaction, it is found that the chemiluminescence spectrum closely resembles the surface glow in the $Na-HgCl_2$ reaction and also the spectrum excited by an electrical discharge in $HgCl_2$.

† (. . .) = gas, [. . .] = solid.

TABLE XXXVII.

Reaction.	Colour of Luminescence.	Position of Maximum Intensity.	Spectral Limits.		Heat of Reaction.
			In $\mu\mu$.	In Kilo-cal.	
$Hg + Cl_2$	green	560 $\mu\mu$	595-300	47·5-94·5	53
$Hg + Br_2$	yellow	590 ,,	670-435	42-65	48
$Hg + I_2$	orange-red	620 ,,	735-480	38·5-59	38

The HgCl molecule must thus be regarded as the emitting centre in the reaction, and similarly HgBr and HgI molecules for the reactions of mercury with bromine and iodine. Little can be said with regard to the reaction mechanisms, except that probably processes of double activation must occur. The heats of reaction given in the final column of Table XXXVII. are considerably smaller than would suffice to excite the shorter wave-lengths observed in the emissions, but double the energies of formation of the dihalide molecules would suffice. Owing to the high concentrations of reactants (and hence of resultants), conditions are specially favourable in these reactions for processes of double activation.

CHEMILUMINESCENCE PRODUCED BY "ACTIVE" HYDROGEN AND BY "ACTIVE" NITROGEN.

"Active" Hydrogen.—In a long discharge tube containing pure dry hydrogen at low pressure there is practically no emission of the Balmer series, but the whole tube is filled with a secondary spectrum for which the emitting units are excited hydrogen molecules. If, however, the hydrogen is contaminated with oxygen or water vapour, the Balmer series shows up brightly in the central portion of the tube, and the above secondary spectrum is now confined to the neighbourhood of the metal electrodes. A tungsten or other metal wire placed in the centre of the tube rapidly becomes red hot and induces in its immediate vicinity the same secondary spectrum of molecular hydrogen. These effects which have been investigated by Wood (*Phil. Mag.*, **42,** 729, 1921 ; **44,** 538, 1922) admit of the following simple interpretation. The hydrogen atoms which are normally formed by electronic impact in the discharge tube are readily adsorbed by the glass surface, upon which association of the atoms to molecular hydrogen can take place. With free adsorption, no appreciable accumulation of hydrogen atoms in the gaseous phase is possible. Oxygen and water vapour, however, are also readily adsorbed by glass, and if present prevent the effective adsorption and association of hydrogen atoms on the surface, so that in their presence a large stationary concentration of atomic hydrogen is obtained in the discharge tube, and the conditions are favourable for intense excitation of the Balmer series. Metals are specially good catalysts for the destruction of atomic hydrogen, and the secondary spectrum always noted in the vicinity of the electrodes or of any metal surface in the tube is either due to molecular hydrogen excited by electronic collisions or is possibly a chemiluminescence resulting from the act of association of hydrogen atoms.

The active or atomic hydrogen may be drawn off from the central portion of a discharge tube and its properties more completely examined. Bonhoeffer (*Z. physikal. Chem.*, **113,** 199, 1924; *ibid.*, **119,** 385, 1926) finds that at ordinary temperatures it reduces a variety of metal oxides, sulphides, and halides, it reacts with the halogens to give the corresponding halogen acids, it is quantitatively converted into molecular hydrogen in a few hundredths of a second by HCl, HBr, H_2S, and CH_3Cl, it hydrogenates oleic acid and forms hydrogen compounds with arsenic, sulphur, and phosphorus. Association to molecular hydrogen is readily catalysed by rough glass surfaces, by metals, and by metal oxides, with intense heating of the catalyst. The activity of active hydrogen is destroyed immediately at liquid air temperatures; normally, however, its life period is about $\frac{1}{5}$ sec., so that binary collisions between hydrogen atoms in the gas phase rarely lead to combination. This is in agreement with the conclusions of Born and Franck regarding the necessity of *ternary* collisions for the production of a stable homopolar diatomic molecule from its constituent atoms.

A stream of active hydrogen drawn from the centre of a discharge tube luminesces in the ultra-violet with an emission corresponding to the well-known water vapour band with maximum at 3064 Å. This band originates from some hydrogen-oxygen compound (possibly the OH radicle itself) whose presence in the stream of active hydrogen is due to the fact that the production of the latter in appreciable concentration requires the presence of traces of oxygen or water vapour. Outside the discharge tube, however, the necessary activation of this emission centre cannot be brought about by electronic impact. Its activation must then result from energy transfer by collision with a hydrogen molecule which is produced by combination of hydrogen atoms; or more probably the emission centre itself functions in the ternary collision necessary for this act of combination. In either case, the available energy, given by the heat of dissociation of hydrogen into atoms, is of the order of 100,000 cal., and from the energetic standpoint is sufficient to produce the observed optical excitation.

The destruction of active hydrogen may under suitable conditions be accompanied by a variety of other luminescence phenomena (cf. Bonhoeffer, *Z. physikal. Chem.*, **116,** 391, 1925). Thus anthracene, phosphorus, quartz, and zinc sulphide phosphors give brilliant band luminescence in the visible when placed in active hydrogen. Again, if a piece of solid sodium is introduced into the path of a stream of active hydrogen, the sodium is rapidly heated to such an extent that it vaporizes, and the gas in its immediate vicinity luminesces with the D line of sodium. Here we are evidently dealing with (*a*) catalytic association of the hydrogen atoms to molecular hydrogen on the surface of the metal with liberation of energy sufficient to vaporise it, (*b*) excitation of the line emission in a free sodium atom (in the gaseous phase) probably as a result of a ternary collision between it and two hydrogen atoms. The same emission is produced in the absence of added sodium if the glass tube through which the active hydrogen flows is heated externally to a temperature slightly below softening. The hot glass is reduced by the atomic hydrogen, as is evidenced by the sublimate of metallic sodium deposited after a short time in the cooler portions of the tube. With potassium in the stream of active hydrogen, Bonhoeffer observed no sensible luminescence. Rubidium and caesium apparently do not give any *line* emission, but in both cases a strong luminescence is observed which on spectral resolution takes the form of a continuous emission band, stretching in the case of caesium from the green into the ultra-violet with maximum intensity in the blue. It is quite possible that with all of the alkali metals the resonance line of the atom (corresponding to the D line of sodium) is actually excited, but escapes observation in every case except that of sodium on account of the wave-length region involved—red to infra-red. Again, the heat of combination of two hydrogen atoms is energetically capable of exciting the atom of any one of the alkali metals to emit the *second* line of its Principal Series. Only for caesium and rubidium, however, would the expected lines fall within the visual range of observation, and in both these cases their presence would be masked by the continuous band emission noted above. This band emission must have its origin either in a diatomic molecule of the alkali metal, or more probably in a metal hydride molecule.

The luminescence obtained with liquid mercury in the stream of active hydrogen is of special interest. Without any external heating, a blue flame appears on the surface of the mercury, the spectrum of which contains both the resonance line 2537 Å and a band system stretching between 450 and 325 $\mu\mu$. The structure of this band system suggests a very small moment of inertia of the radiating structure, which is, therefore, in all probability a mercury hydride molecule. On the other hand, the seat of emission of the resonance line is the mercury atom itself, yet the two emissions apparently cannot be obtained independently of one another. Thus a photograph of the luminescence taken with a light filter which transmits the line 2537 Å only is identical in form and general characteristics with that obtained without the light filter. Again, mercury vapour itself gives no luminescence either of the band or of the resonance line with active hydrogen, and indeed if the liquid mercury in a stream of active hydrogen be gradually heated the luminescence over its surface disappears, apparently because the hydrogen atoms can no longer diffuse to the liquid surface against the stream of mercury vapour. From these observations, Bonhoeffer concludes that the luminescent hydride can be formed only by heterogeneous reaction between hydrogen atoms and the liquid mercury. This process is probably slightly exothermic, but the resulting hydride molecule can hardly leave the surface with any appreciable excess of internal or translatory energy. It must then be excited to luminescence in the gaseous phase by collision with some system rich in energy which is available for transfer. Nothing very definite can be said about the act of excitation itself. Bearing in mind the fact that energy transfer up to 87 kilo-cal. (corresponding to 325 $\mu\mu$, the upper limit of the luminescence band) is necessary, the following possibilities suggest themselves: (*a*) a binary collision between the mercury halide molecule and a metastable mercury atom which has previously been excited to the 2^3P_0 level by a ternary collision $H + H + Hg \rightarrow H_2 + Hg(2^3P_0)$; (*b*) a ternary collision $HgH + H + H \rightarrow HgH$ (activated) $+ H_2$. The first possibility requires that the energy of dissociation (D_{H_2}) of hydrogen into atoms should be capable of displacing the valency electron of the mercury atom from the normal to the 2^3P_0 orbit, and this is just possible if we accept the rather high value $D_{H_2} = 107$ kilo-cal. recently given by Bodenstein and Jung (*Z. physikal. Chem.*, **121,** 127, 1926). It further requires that active hydrogen should be destroyed, at least partially, by mercury vapour. Regarding these two necessities we have no experimental evidence.

As regards the excitation of the resonance line 2537 Å, which is coupled in some way with the band emission, this cannot take place by a ternary collision between a mercury atom and two hydrogen atoms. Such a process would constitute a reversal of the dissociation of hydrogen into atoms sensitised by activated mercury atoms in the 2^3P_1 state; this is impossible, at least at ordinary temperatures, on account of the energy transfer required, namely 112 kilo-cal., and actually there is no evidence of its occurrence in mercury vapour and active hydrogen in the absence of liquid mercury. Since no single act of energy transfer from a luminescent hydride molecule to a normal mercury atom is likely to result in activation of the mercury atom to the extent of 112 kilo-cal., an explanation of the emission of the 2537 Å line must be sought in accumulation of energy in stages *via* a metastable hydride molecule or a metastable mercury atom. Another possibility lies in a collision between a normal and an excited hydride molecule—

$$HgH + HgH \text{ (activated)} \rightarrow H_2 + Hg + Hg(2^3P_1).$$

While a decision between such possibilities cannot be made, there is little doubt that the process under consideration requires some such complex mechanism as above suggested.

"Active" Nitrogen.—It was shown by E. P. Lewis (*Astrophys. J.*, **12,** 8, 1900) that a yellow after-glow is produced in nitrogen when a condensed electrical discharge is passed through the gas at low pressures. Strutt (Lord Rayleigh) (*Proc. Roy. Soc.*, 1911-1923; *J.C.S.*, **113,** 200, 1918) made a careful study of the characteristics of the luminescence and also of the chemical reactivity of the "active" nitrogen. The interpretation of his results as well as those of other investigators has aroused much discussion, and a large amount of material has been published on this subject. Two theories of the after-glow have been suggested. According to the one, nitrogen atoms are formed in the discharge tube; these combine, probably as a result of a ternary collision ($N + N + N_2$), forming excited nitrogen molecules which emit the glow. The emission according to this view is a *chemiluminescence*, as in the case of active hydrogen. According to the other theory, metastable N_2 molecules of relatively long life are formed in the discharge tube, and these eventually emit the glow. Recent work (cf. Willey, *J.C.S.*, p. 2831, 1927; Bonhoeffer and Kaminsky, *Z. physikal. Chem.*, **127,** 385, 1927; B. Lewis, *J. Amer. Chem. Soc.*, **50,** 27, 1928) would seem to indicate that the active form of nitrogen is non-homogeneous and that nitrogen molecules in various states of activation as well as atoms are present. There are reasons for presuming that the luminescence is essentially a chemiluminescence phenomenon, i.e. that the first theory is the correct one. Analysis of the banded glow spectrum by Birge and Sponer (*Physical Rev.*, **28,** 259, 1926) indicates that the energy level of the emitting N_2 molecule is about 11·5 volts above that of the normal molecule, and that this level corresponds to the energy of combination of two nitrogen atoms. Further, it has been demonstrated by Strutt (*Proc. Roy. Soc.*, **91**A, 303, 1915), Angerer (*Physikal. Z.*, **22,** 97, 1921), and Bonhoeffer and Kaminsky (*loc. cit.*) that the process causing the emission is bimolecular with respective to the "active" gas. The work of the last-mentioned authors, however, also draws attention to a difficulty involved in the "atom" hypothesis, as they found that the collisional process inducing the glow is not a three-body collision.

THE OXIDATION AND LUMINESCENCE OF PHOSPHORUS.

The slow oxidation of phosphorus probably forms the earliest recognised example of chemiluminescence. It also presents other features of interest and has been studied by many investigators,* though, owing to the complex nature of the change, a clear picture of its mechanism has not yet been arrived at. The most striking characteristic of the reaction is its highly exothermic nature, and to this must be related certain secondary effects associated with the oxidation, such as chemiluminescence, the formation of gaseous ions, and, in presence of moisture,† the formation of ozone and of hydrogen peroxide.

Yellow phosphorus in air or in oxygen under reduced pressure oxidises at ordinary temperatures and the process is accompanied by the emission of a greenish luminescence. If the partial pressure of oxygen is increased beyond a certain limit, the chemiluminescence is extinguished though slow oxidation probably still takes place. For pressures of oxygen near this limiting one, the continuous glow may become intermittent. Similar behaviour may also be observed when the oxygen content of the gas is low, in which case the stationary gas phase above the phosphorus may assume a striated appearance similar to that in a discharge tube excited at low pressure, i.e. periodic propagation of waves of luminosity through the gas phase may take place. In addition to a maximum critical pressure of oxygen above which the glow is extinguished, there is also a lower critical oxygen content (10^{-2} mm.) below which reaction cannot be detected. The vapours of a number of organic compounds (e.g. acetone, ethylene, ether) exert a very strong inhibiting effect on the oxidation of phosphorus, and in their presence the glow is either reduced in intensity or disappears completely. In small quantities, these vapours lower the maximum critical pressure of oxygen. Many striking experiments on the periodic luminosity and the action of inhibiting agents are described by Rayleigh (*Proc. Roy. Soc.*, **99**A, 372, 1921 ; **104**A, 322, 1923) and by Waran (*Phil. Mag.*, **45,** 1132, 1923.)

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* For literature references and a more complete discussion of the reaction than is possible here, see Bäckström, *Medd. K. Vetenskapsakad. Nobel-Inst.*, **6**, No. 16, 1927.

† Baker (*J.C.S.*, **47**, 349, 1885) has shown that the presence of water vapour is requisite for oxidation of phosphorus to occur.

In the oxidation of phosphorus at ordinary temperatures, both phosphorus pentoxide and phosphorus trioxide result. Scharff (*Z. physikal. Chem.*, **62,** 179, 1908) and others have shown that the phenomena accompanying the auto-oxidation of phosphorus trioxide are very similar to those occurring when phosphorus itself is oxidised. Essentially the same luminescence is observed which may be continuous or intermittent according to the conditions, there is also an upper critical oxygen pressure for the glow, and those vapours which inhibit the luminescent emission from oxidising phosphorus also inhibit the glow of the trioxide. The claim that ozone formation accompanies the oxidation of P_4O_6 has been made by certain investigators (cf. Downey, *J.C.S.*, **125,** 347, 1924) but is denied by others.

The spectrum emitted by phosphorus oxidising at ordinary temperatures is continuous in the visible with a maximum in the green ; in the ultra-violet it comprises a large number of narrow bands lying in five or six groups between 340 and 240 $\mu\mu$. Essentially the same band spectrum in the ultra-violet has been obtained by Downey and Emeléus (*J.C.S.*, **125,** 2491, 1924) when phosphorus burns in air under reduced pressure (flame temperature 125° C.) or in enriched air with a flame temperature of 800° C. ; in the high temperature flame, however, each group of bands coalesces into a single broad band. Emeléus (*ibid.*, **126,** 1362, 1925) further finds that phosphorus trioxide or phosphine burning in air or oxygen each gives an ultra-violet band emission identical in its main features with that of the oxidation of phosphorus. From these results it appears probable that the molecular species emitting the light is the same in all cases. Minor variations in the relative intensities in the bands would thus be due, not to differences in the emission centres, but to the different physical conditions of excitation of the centre. For example, in the glow spectrum of phosphorus or phosphorus trioxide, the intensity of the band system at 327 $\mu\mu$ is relatively less than that obtained when the element, oxide, or hydride burns under reduced pressure, that is, when the oxidation takes place at a higher temperature. According to Downey (*J.C.S.*, **125,** 347, 1924), the spectrum of the glow of phosphorus extends into the region 180-120 $\mu\mu$, that fraction transmitted by fluorite being capable of ionising air. Busse (*Ann. Physik*, **82,** 873, 1927; **83,** 80, 1927), however, does not confirm this result.

Petrikaln (*Z. Physik*, **22,** 119, 1924) suggested that the emitting unit in the glow of phosphorus is the molecule of pentoxide, and Emeléus and Purcell (*J.C.S.*, p. 788, 1927) also arrived at the conclusion that the glow had its origin in an oxide molecule. They showed that the spectrum produced by passing a discharge through phosphorus pentoxide vapour corresponds in part with the band spectrum of the glow of phosphorus. Johnson (cf. Emeléus and Purcell, *J.C.S.*, p. 628, 1928) pointed out, however, that the spectrum of the discharge through the pentoxide is identical with the band spectrum of singly ionised oxygen; it might thus be possible for the glow spectrum of phosphorus to be due to oxygen. More recently Petrikaln (*Naturwiss.*, **12,** 205, 1928) finds that phosphorus trioxide activated in various ways gives the same band emission as is obtained in the glow of phosphorus and phosphorus trioxide, and that the band group at 327 $\mu\mu$ present in the phosphorus glow does not appear in the spectrum from P_2O_5 unless the latter contains P_2O_3 as an impurity; hence he concludes that it is the trioxide molecule which emits in the chemiluminescent oxidation of phosphorus.

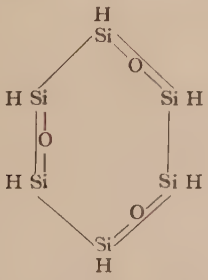
The heat evolved in the reaction $2P + \frac{5}{2}O_2 = P_2O_5$ has the extraordinarily high value of 370,000 cal.; the intermediate stages in the reaction are not known, however, so that it is not possible to estimate the magnitude of the units of energy available for purposes of activation. Bäckström (*loc. cit.*) considers that, since the molecular weights of the element and its two oxides correspond to the formulæ P_4, P_4O_6, and P_4O_{10}, the reaction takes place in five stages each involving the addition of a molecule of oxygen, and that each stage liberates about 150,000 cal. From the energetic standpoint, this is equivalent to 190 $\mu\mu$, thus accounting for the magnitude of the maximum frequency detected with certainty in the emission. Emission of light of this wave-length could account also for the formation of ozone which is an accompaniment of the reaction.

The view now generally held with regard to the nature of the oxidation of phosphorus is that it is a process whose rate depends essentially on the transference of energy liberated in a primary process to neighbouring oxygen or phosphorus molecules, which thereby become reactive. The process is then a "chain" reaction (cf. p. 447) in which activated molecules resulting in one stage of the reaction transfer by collision their excess energy to fresh reactant molecules. This view is supported by the fact that the reaction is very sensitive to the action of inhibitors—a characteristic of "chain" processes in general—the retardation being ascribed to the capacity of inhibitor molecules for deactivating "hot" reactant molecules. Thus oxygen, though necessary for reaction, is an inhibitor when present in excess, its inhibiting action probably being associated with its conversion into ozone. According to Bäckström, the light emitted during the reaction is absorbed by phosphorus, which thereby attains enhanced chemical reactivity. If this is the case, a primary thermal process is followed by a secondary photochemical one, and reaction " chains " are propagated not only by collisional but also by radiational transfers of energy. The " chain " theory has recently received strong support from the work of Semenoff (*Z. Physik*, **39**, 547, 1926 ; **46,** 109, 1927 ; **48,** 571, 1928), who has demonstrated how the theory predicts critical limits of pressure for the reaction. It should also be mentioned that the oxidation of phosphorus is one of the very exothermic processes in which traces of water vapour play an important part.

Other chemiluminescent oxidations whose mechanisms probably are similar to that of the oxidation of phosphorus are the slow burning of arsenic (Emeléus, *J.C.S.*, p. 783, 1927) and the phosphorescent combustion of sulphur (Emeléus, *J.C.S.*, p. 1942, 1928 ; Semenoff, *loc. cit.*). Other auto-oxidation reactions which also appear to be chain reactions are discussed in Chapter XII.

CHEMILUMINESCENCE OF UNSATURATED SILICON COMPOUNDS.

The remarkable luminescence effects described under this heading have been very exhaustively studied by Kautsky and his co-workers. When calcium silicide is treated with hydrochloric acid, hydrogen is liberated and, depending upon the conditions of working, silicon compounds of various degrees of oxidation are obtained. The end product of progressive oxidation of the mixture is silicic acid, but between this and the calcium silicide there lie (1) siloxen, a compound of composition $Si_6O_3H_6$, and for which the structural formula



has been suggested, (2) silical hydroxide or oxy-siloxen $Si_6O_3H_5OH$, and (3) leuco-compounds of as yet undetermined composition, representing stages of oxidation between oxy-siloxen and silicic acid.

Siloxen and these leuco-compounds are colourless, oxy-siloxen however is dark-red and the salts which it gives with acids ($Si_6O_3H_5Cl$, etc.) are usually bright yellow in colour.

These oxygen derivatives of silicon have a peculiar morphological structure (Kautsky and Herzberg, *Z. anorg. Chem.*, **147,** 81, 1925). Including the end product of their oxidation—silicic acid—they are all built up of very thin lamellar flakes lying upon one another like the leaves of a book. The flakes are extremely porous, and thus the adsorption capacity of these substances is very great. They present a very large surface to any oxidising medium, liquid or gaseous, so that oxidisation readily occurs throughout the whole mass. Because of their high reactivity and insolubility, the individual compounds are difficult to isolate in the pure state. The preparation usually employed in experiments on chemiluminescence by Kautsky is a yellow mixture of siloxen and oxy-siloxen, and is called " silikone " in the literature. With increasing amount of oxy-siloxen in silikone the colour of the substance changes from yellow through orange to red. With decreasing amount of oxy-siloxen in mixtures of this with its further oxidation products (leucones) the colour changes in the opposite sense. This continuous change in body colour with the percentage of the dark-red oxy-siloxen present is probably due to dichromatism on the part of oxy-siloxen, which absorbs strongly in the green and blue. The colour gradations are important in relation to the colours of the chemiluminescence obtained by oxidation of the various mixtures.

Siloxen or silikone may be oxidised at ordinary temperatures by air or oxygen, more rapidly by liquid oxidising reagents such as potassium permanganate in acid solution, chromic acid, hydrogen peroxide, etc. Kautsky and Zocher (*Z. Physik*, **9,** 267, 1922) find that oxidation of practically pure siloxen produces at first only a very feeble greenish chemiluminescence. As, however, the system becomes richer in oxy-siloxen, the intensity of the luminescence rapidly increases, and reaches a maximum when the body colour of the silikone is yellow. Simultaneously the colour of the emission changes through greenish-yellow to yellow. With further increase in the percentage of oxy-siloxen present, the intensity of the chemiluminescence falls off and the colour of the emitted light passes through orange to red.

Starting with the pure oxy-siloxen and treating with hot water, oxidation to the colourless leucones takes place. The colour of the system changes progressively with time from dark red through bright red, orange, yellow, and yellowish-green to white, and simultaneously the mixture emits a luminescence whose colour changes through the same gradation. The intensity of the chemiluminescence again reaches a maximum when the substance colour is yellow. The leuco-compounds which are finally obtained give no visible luminescence on further oxidation.

The apparent dependence of the colour of the chemiluminescence for both oxidation processes solely on the relative amount of oxy-siloxen present makes it very probable that the emission centre is the oxy-siloxen molecule itself. No satisfactory explanation of the maximum observed in the intensity of the luminescence has yet been given ; but it suggests itself that this may be due to the combined action of three factors—(1) the number of molecules of oxy-siloxen excited will be the greater the greater its concentration, (2) the energy available for excitation will depend upon the amount of oxidisable substance present, and (3) the more oxy-siloxen is present, the greater is the probability of reabsorption and degradation of the radiation emitted in the bulk of the oxidising system. Kautsky and Zocher draw attention to the formal similarity between the behaviour of the intensity of chemiluminescence with increasing concentration of oxy-siloxen and that of the intensity of fluorescence of a dyestuff in solution with increasing concentration of dyestuff (cf. p. 312).

The spectrum of the chemiluminescence obtained in the above oxidation reactions consists of a continuous band stretching from the red to the yellow-green or green, with a maximum which shifts towards shorter wave-lengths as the colour of the chemiluminescence alters from red to green. The absorption spectrum of oxy-siloxen, on the other hand, lies further towards the violet with maximum in the blue-green, so that the chemiluminescence spectrum really stands in much the same relation to the absorption spectrum of the oxy-siloxen as does the fluorescence spectrum of a substance to its absorption spectrum. The identification of the oxy-siloxen molecule as the emitting unit in the chemiluminescence is further borne out by the observations described below.

Photoluminescence of Siloxen and Oxy-Siloxen.—Many of the oxidation processes of siloxen to oxy-siloxen and of oxy-siloxen to leucones are photochemical reactions, the limiting photochemical wave-lengths lying in the blue and green portions of the spectrum. The photo-oxidation of siloxen itself belongs to the class of sensitised photochemical reactions. By illumination with diffuse daylight of a nearly colourless mixture of siloxen, ethyl iodide, and water, the rate of photo-oxidation increases rapidly as the coloured oxy-siloxen is formed, the latter substance, on account of its large absorption capacity in the visible, acting as light sensitiser for the colourless siloxen. Simultaneously with the occurrence of the photo-oxidation, the system luminesces with light of colour which varies from green through yellow and orange to red as the amount of oxy-siloxen present increases. This luminescence is much brighter than the chemiluminescence which would be emitted by the same system undergoing thermal oxidation. Again, the photo-oxidation of moist oxy-siloxen to the leuco-compounds is accompanied by an emission which changes progressively in colour from red through orange and yellow to green with diminishing oxy-siloxen content. Apparently, then, this photoluminescence, which is formally a fluorescence of the oxidising system, is identical in type with the chemiluminescence produced by thermal oxidation. However, the fluorescence does not necessarily owe its origin to the occurrence of the photochemical reaction, but may be a simultaneous and independent phenomenon. Kautsky and Zocher have tested whether the fluorescence can be excited by the photochemically active light *in the absence of chemical change*, by illuminating oxy-siloxen at the temperature of liquid air. Under these circumstances, a very much brighter fluorescence is obtained than at room temperatures, and this in spite of the fact that photochemical action is no longer detectable. It follows, then, that whilst a part of the photoluminescence at ordinary temperatures *may* be of the nature of a photochemiluminescence, the bulk of the effect is a true fluorescence of the oxy-siloxen and is independent of the occurrence of chemical change.

Besides the enhanced fluorescence, Kautsky and Zocher have also observed a phosphorescence of oxy-siloxen at low temperatures. This is obtained in more appreciable intensity on warming a mixture of oxy-siloxen and alcohol which has previously been illuminated at liquid-air temperatures. Cathode rays also produce a light emission. In all cases the colour of the luminescence is the same as the body colour of the material and as the colour of the chemiluminescence which would be produced under corresponding conditions of temperature and oxy-siloxen content.

This independence of the colour of the luminescence on its mode of excitation—whether by chemical action, by absorbed radiation, or by cathode rays—substantiates the conclusion arrived at from the characteristics of the chemiluminescence itself that the emitting centre is the oxy-siloxen molecule. With the photo- and cathode-luminescence it is possible that the oxy-siloxen molecule which emits is the same molecule as is excited by the primary process—absorption of radiation or collision with β-particles. Also, in the chemiluminescence obtained by thermal oxidation of siloxen, the resultant oxy-siloxen molecule may be the actual emitting unit; but in the oxidation of oxy-siloxen itself, the act of emission must obviously be preceded by transfer of energy from the energy-rich resultant leucone to a non-reacting neighbouring oxy-siloxen molecule. This being so, Kautsky and Zocher consider it probable that in all cases this same type of energy transfer from activated to non-activated molecules takes place before luminescence.

Sensitised Chemiluminescence.—Very direct evidence in favour of energy transfer from reaction products to emission centres has been obtained by Kautsky and co-workers (*Z. Elektrochem.*, **29,** 308, 1923; *Z. Physik*, **31,** 60, 1925; *Trans. Faraday Soc.*, **21,** 591, 1926) from a study of the luminescence excited in certain foreign substances present during the oxidation of silicon compounds. In order that the observations should not be complicated by chemiluminescence of the silicon compounds themselves, silico-oxalic acid was chosen as the most suitable substance for oxidation. This colourless compound is readily oxidised by potassium permanganate in acid solution, but it gives no chemiluminescence and no coloured reaction products. It possesses the same morphological structure and abnormal surface development as the other unsaturated silicon compounds, and as a consequence is equally efficient in adsorbing gases and dissolved substances from solution. With basic fluorescent dyes such as rhodamine-B, rhodamine sulphonate, and isoquinoline red, strongly coloured adsorbed films are obtained which also fluoresce to an appreciable extent, and with a fluorescence spectrum identical with that of the dye in solution. With such an adsorbed film, we have optimum conditions for the emission of a luminescence by the dye, induced not by exposure to radiation but by oxidation of the underlying silico-oxalic acid and transfer of the liberated chemical energy from the reaction products to the neighbouring dye molecules.

In agreement with expectation, when any of these adsorption complexes is treated with acid permanganate solution, a bright chemiluminescence is produced. The spectrum of this is identical with the fluorescence spectrum of the dye itself, so that there is no ambiguity regarding the identity of the emitting substance. The objection might be raised that, since the dyestuff itself is partly oxidised along with the silico-oxalic acid, the chemiluminescence of the dye might be due to its own oxidation, just as it has been suggested that the fluorescence of organic compounds is conditioned by their photochemical destruction by the exciting light (see Chapter V.). This possibility, however, is disposed of by Kautsky's observation that, with an adsorbed film of rhodamine or rhodamine sulphonate not on silico-oxalic acid but on silicic acid (which has the same morphological structure as silico-oxalic acid, but is *not* oxidised by potassium permanganate), the dye itself may be oxidised with permanganate without any luminescence being observed. The chemiluminescence of the dye is therefore induced not by its own oxidation but only by oxidation of the surface layer of silico-oxalic acid contiguous to the adsorbed film.

Such sensitised chemiluminescence as this in a heterogeneous system is obviously the analogue of several cases already dealt with for homogeneous systems, for example, the excitation of the mercury resonance line in the gaseous system Hg—Na—Cl_2, where the mercury atom is activated by collision with a reaction product of the sodium-chlorine reaction. They are all examples of the reverse phenomenon to that of sensitised photochemical action.

The exact mechanism of energy transfer in the case of the heterogeneous system is naturally unknown. It is clear, however, that the reaction product rich in energy and the recipient dye molecule must be close together for energy transfer to be at all possible. Next to solid solutions, the remarkable porous structure of the unsaturated silicon compounds offers the best possible conditions for juxtaposition on an extensive scale of reaction and luminescence centres.

OTHER CHEMILUMINESCENT REACTIONS.

Two important groups of organic processes accompanied by chemiluminescence are the oxidation of Grignard reagents and their decomposition by chloropicrin. The first observation of luminosity associated with a Grignard compound was made by Wedekind (*Physikal. Z.*, **7,** 805, 1906) who found that phenyl magnesium iodide gives an intense green emission when reacting with chloropicrin (the Wedekind reaction)—

$$3C_6H_5MgI + CCl_3 . NO_2 \rightarrow (C_6H_5)_3C . NO_2 + 3Mg(I)Cl.$$

Since then chemiluminescence has been observed with a number of other organo-magnesium compounds, not only when reacting with chloropicrin, but also when exposed to air or oxygen either in the solid state or in ethereal solution. Systematic investigations have been carried out recently by Lifschitz and Kalberer (*Z. physikal. Chem.*, **102,** 393, 1922) and by Dufford, Evans, and associates (*J. Amer. Chem. Soc.*, **45,** 278, 2058, 1923; **47,** 96, 1925). The last-named authors give a list of over forty Grignard compounds of varied character, ethereal solutions of which luminesce on oxidation. Noteworthy examples in respect of intensity of emission are the phenyl magnesium halides, *p*-bromo- and *o*-, *m*-, and *p*- chloro-phenyl magnesium bromides.

The colour of the chemiluminescence is almost invariably green to blue, and when analysed consists of a single broad emission band in the upper region of the visible spectrum. With the same Grignard compound, the emission obtained by oxidation is not identical with that given by the Wedekind reaction. Generally the chemiluminescence in the latter case is green in colour, and is only obtained for Grignard compounds which give a greenish-blue or blue luminescence on oxidation. According to Dufford and Evans, a necessary condition for light emission is that the magnesium atom should be directly attached to an unsaturated carbon atom. Lifschitz and Kalberer agree with this in so far as they find that no compound in which the magnesium is linked directly to a saturated aliphatic carbon atom gives rise to luminescence when oxidised in ethereal solution; but they state that the condition does not apply to oxidation of the solids, both aromatic and aliphatic Grignard reagents luminescing under these circumstances. Of the aromatic Grignard compounds, those with *para* substitution in the benzene ring give the most intense light emission. Another chemical factor which appears to influence the intensity of the luminescence is the nature of the halogen atom which is linked to the magnesium; for the same type of compound, the intensity of the luminescence accompanying reaction with oxygen decreases, but that of the corresponding Wedekind reaction increases, as we pass from chlorine to iodine. The brightest emission is given by reaction with oxygen, but certain organic peroxides also produce a faint luminescence. On the other hand, hydrogen peroxide, nitrogen peroxide, water, and other substances which react much more violently with Grignard compounds produce no visible light emission. So far as solvent medium is concerned, ethyl ether is usually employed, but the chemiluminescence is equally bright using other ethers or dimethyl aniline as solvent. In the latter case the chemiluminescence is brown in colour. There appears to be an optimum concentration of the Grignard compound in solution, above which concentration the intensity of the emission decreases.

The reactions of Grignard compounds with oxygen and with chloropicrin are rapid and highly exothermic, but these conditions, though necessary, are not sufficient to ensure the emission of light. The slight differences between the heats and rates of reaction of the aliphatic and aromatic compounds in ether solution are inadequate to explain the difference in their behaviour as regards luminescence. Again, the decomposition of phenyl magnesium bromide by water is more rapid than and just as exothermic as its decomposition by chloropicrin, yet only the latter reaction is luminescent. This last result would suggest that the light emission is conditioned by the products of reaction rather than by the reactant itself.

A factor which should be equally as important as rate of reaction or heat of reaction in determining whether or not a given process should be accompanied by visible chemiluminescence is the capacity of some component of the system to give a visible *fluorescence*. Such a capacity would indicate states of excitation of the molecule which could conceivably be produced also by means of the energy of reaction and from which the molecule could revert to its normal state with emission of light. Actually, Dufford and Evans find that many Grignard compounds do fluoresce in the visible when illuminated with near ultra-violet light and that their oxidation products possess the same property to an even more marked degree. This ability to fluoresce is not confined, however, to those Grignard compounds or their oxidation products which give chemiluminescence, hence the fluorescence capacity cannot be accepted as a sufficient criterion for chemiluminescence, even when supported by a high rate and a large heat of reaction.

The brightest fluorescence appears to be given by the oxidation products of those reactions which give the brightest chemiluminescence. Again *p*-bromo-phenyl magnesium bromide, which oxidises with a very bright luminescence, is not itself notably fluorescent, but its oxidation products fluoresce brilliantly. It is very probable, then, that in this case and in others a reaction product and not the reactant itself is the emission centre of the chemiluminescence. The colour of the fluorescence of the reaction products is usually green to blue, but, unlike the case of oxy-siloxen, the spectra of the fluorescence and of the chemiluminescence do not appear to be identical. Comparison is complicated by the fact that sometimes, as with *p*-bromo-phenyl magnesium bromide, there is in the mixture of oxidation products at least two substances which fluoresce with light of different colours. Much useful work still requires to be done, therefore, in the direction of identifying and isolating the reaction products which fluoresce. It would be interesting to test whether a particular reaction product could be sensitised to luminescence by energy transfer from the resultants of another reaction. For example, would a reaction mixture of a saturated aliphatic Grignard reagent and the oxidation products of *p*-chloro-phenyl magnesium bromide (which latter fluoresce brilliantly in near ultra-violet light) give a chemiluminescence when oxidised with oxygen? By such experiments as this might be decided the question as to whether, in the chemiluminescent oxidation of a Grignard compound, the activated resultant molecule itself luminesces or whether it induces luminescence in another resultant molecule through energy transfer by collision.

CHAPTER VII.

PHOTOCHEMICAL REACTIONS.

GENERAL.

A SYSTEM receiving from an outside source radiant energy the frequency of which is almost entirely absent in the temperature radiation of the system itself may utilise the energy received in several ways. It may simply convert the absorbed radiation into heat, it may reradiate it as resonance radiation, fluorescence, or phosphorescence, or the energy may give rise to chemical changes in the system. In the previous Chapters, the first and second classes of phenomena have been discussed; we must now deal with the third, photochemical reactions proper, in which detectable changes in the chemical constitution of the system are brought about. In most photochemical investigations, the radiation employed has been visible or ultra-violet light; it is, however, unnecessary to confine photochemical reactions to those initiated or accelerated by radiation within these ranges; we may conveniently include in our definition the whole of the electromagnetic spectrum, including *X*-rays and infra-red radiation. Experiment shows that all types of chemical changes may be brought about by light; we have oxidations and reductions, decompositions (photolyses), addition reactions, polymerisations and isomerisations, etc. Further, light can exert a very marked accelerating effect on certain reactions which proceed in the dark at an immeasurably slow speed, and it has been claimed that instances occur in which light acts as a negative catalyst, i.e. it may retard a reaction already in process.* Many photochemical reactions, in especial organic photo-reactions, occur in a quite *specific* manner; they have so far not been effected in the dark under comparable conditions. Thus, the hydrolysis of acetone by ultra-violet light takes place according to Ciamician and Silber (*Ber.*, **36,** 1582, 1903) in the manner

$$CH_3 . CO . CH_3 + H_2O \rightarrow CH_4 + CH_3 . COOH,$$

a reaction which does not occur in absence of light, though certain other ketones may be hydrolysed in a similar manner in the presence of strong alkali. The study of photo-processes is in many respects analogous to that of thermal processes. All the factors which influence the velocity of thermal reactions have to be taken into account when dealing with photochemical reactions. In particular, such variables as the concentrations of reactants, temperature, pressure, solvent, concentrations of catalysts and inhibitors, etc. may exert a marked effect on the velocity, and careful examination of these effects is requisite for a thorough investigation in each reaction. In both cases, thermal and photochemical, induction periods may be found, as also may be the remarkable catalytic effect of traces of water, no reaction taking place after sufficient desiccation. In the case of photochemical reactions, however, we have the additional factor, the supply of energy from the external light source, to take into account. This entails consideration not only of the intensity and quality of the light employed, but also of the variation of the intensity of radiation at different points in the reacting system. From the experimental point of view, therefore, photochemical reactions are not so amenable to exact investigation as thermal reactions, especially as the control and determination of the additional factor—the radiation—frequently involve a difficult technique. In thermal reactions the chief hindrances to exact investigation are the presence of traces of catalysts and variations in their activity; in photochemical reactions these effects may also be specially pronounced and in addition we have variations (often unavoidable) in the optical conditions. These difficulties are made manifest by conflicting statements with regard to the same reaction frequently found in the literature, and also by comparatively poor reproducibility of results. A re-investigation of a photochemical process, with application of improved methods of attack, often leads to new developments and often establishes the importance of some factor previously unsuspected or neglected. Also difficulties abound in the interpretation of experimental data, i.e. in the formulation of a satisfactory reaction mechanism. Occasionally, it is found difficult to furnish any theory in explanation of the available results; at other times, however, the choice of several alternative hypotheses seems open, with only considerations of relative probability to act as a guide. We must therefore recognise that many of our hypotheses are at best only provisional; they are useful in suggesting fresh lines of work, but must be abandoned or modified as fresh experimental evidence accrues.

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* See, however, p. 666.

There has been published in the last hundred years a very large amount of material dealing with the action of light on photosensitive systems. Such work has been fairly completely summarised by Eder (*Handbuch der Photographie*, Vol. I., Part 2) and especially by Plotnikow (*Lehrbuch der Photochemie*). As has been pointed out by Weigert (*Ahrens Sammlung*, **17,** 183, 1912), however, much of this material appears at present to possess very little theoretical interest. This applies in particular to organic photosyntheses in which the interest of the investigator lay in the yield of his resultant product, rather than in the nature of the process itself. The same applies, though perhaps to a lesser extent, to much of the work dealing with photography, whose practical development had—at least up to the beginning of the present century—far outrun developments on the theoretical side. In the following pages, we have omitted consideration of material from these sources except in so far as it is judged to be of interest from the purely theoretical standpoint. The intensive photochemical work of the last few years has dealt to a marked degree with theoretical aspects of the subject, and it is primarily this modern work that we have chosen for discussion.

HISTORICAL.

Although it had been recognised since the time of Aristotle, and probably much earlier, that light plays an essential part in such processes as the growth of plants and the bleaching of naturally occurring dyes, it does not appear that any systematic photochemical investigations were carried out until the beginning of the eighteenth century. In 1727 the German physician J. Schultze discovered that the white carbonate of silver blackened in the light; the sensitivity to light of silver chloride had indeed been previously noted by Robert Boyle, but had been attributed to the action of the atmosphere. The discovery of Schultze was independently made in 1757 by Beccarius (the silver salt being the chloride), while in 1777 the Swedish chemist Scheele described the results of his work on the same photochemical process. He established the important fact that the effect of the solar spectrum on paper covered with silver chloride is a maximum in the violet. A few years later, Senebier (*Mémoires physico-chimiques sur l'influence de la lumière*, Geneva, 1782) published an account of systematic investigations on the action of sunlight on plants and plant pigments, and also of experiments devised to study quantitatively the effect of different wave-lengths on silver chloride paper. Further work on the photo-assimilation of carbonic acid was carried out by de Saussure (1790), who also constructed the first actinometer, dependent on the action of light on chlorine water, a reaction previously discovered by Berthollet. In 1801 two discoveries were made which were destined to exert a profound influence on the future of photochemistry. Cruickshank (*Nicholson's Journal*, [i], **5,** 202, 1801) found that light exerts a catalytic influence on the combination of hydrogen and chlorine, a reaction which has since attracted the attention of a large number of investigators and which still presents many baffling features. The other notable discovery was that of Ritter, who found that the action of spectrally decomposed light on silver chloride extends beyond the limits of the visible violet portion and who therefore inferred the existence of ultra-violet rays. (The existence of the infra-red spectrum had already been noted a year previously by Herschel). Further work on photochemical reactions involving chlorine was done by Davy and Faraday (chlorination of marsh gas, union of CO and Cl_2, etc.), Gay-Lussac and Thenard (1809), Seebeck (1810), and Dalton (1811). The hydrogen-chlorine reaction was studied quantitatively by Draper (1841-1845) and especially by

Bunsen and Roscoe (*Ostwald's Klassiker*, **34-38**), whose well-known work on the dynamics of the process was begun in 1854. In the meantime (1817), Grotthus had enunciated the first general law of photochemistry, namely, that only absorbed radiation is effective in producing chemical change, and had advanced a theory of the chemical action of light. Little attention, however, was paid to Grotthus's work, and the determinative influence of absorption on photochemical processes was re-discovered by Draper (*Phil. Mag.*, [iii], **19,** 195, 1841), on the basis of experiments on the combination of hydrogen and chrorine in the light.

The practical application of the light-sensitivity of silver compounds for photographic purposes, based on the discoveries of Schultze, Scheele, Wedgwood and Davy (1802), and Seebeck (1810), was effected by Daguerre and Nièpce, whose work extended from 1814 to 1830 and resulted in 1838 in the successful permanent fixing of light pictures by the production of Daguerrotypes. Talbot replaced the silver plates used in Daguerre's process by light-sensitive paper and further progress was made by Nièpce de St. Victor, who introduced collodion films, and by the production of silver bromide-gelatine films by Maddox (1871) and Bennett (1878). The possibility of photographic reproduction of colour was demonstrated by Lippmann (1891) and Joly (1894). A discovery of theoretical as well as practical significance was that of optical sensitisation made by H. Vogel (*Ber.*, **6,** 1305, 1873); who found that by addition of certain dyes to photographic plates the latter are made sensitive to portions of the spectrum not absorbed by silver bromide.

The rapid and successful development of photography in the latter half of the past century tended perhaps rather to delay the scientific study of photochemistry, but the first quarter of the present century has coincided with new developments and new interest in the theoretical aspects of the subject. This is very largely due to the introduction of the Quantum Theory by Planck, and its application by Einstein to photochemistry in what is now known as Einstein's Law of Photochemical Equivalence. According to this, the absorbing substance absorbs light in quanta, and the primary process in photochemical change is the absorption of one quantum $h\nu$, of frequency ν, by each absorbing molecule. The observed photochemical reaction is a consequence of the enhanced chemical reactivity of the absorbing molecules, which enter into secondary chemical processes yielding the final reaction products. Much experimental work has been carried out since 1912 to test the validity of the Einstein relation. The most important is the series of classic researches of E. Warburg (*Z. Elektrochem.*, **26,** 54, 1920) whose work has been instrumental in refocussing attention on the mechanism of photochemical change. Other important work before and since the appearance of Einstein's Law has been carried out in the laboratories of D. Berthelot, Bodenstein, Chapman, Ciamician, J. Franck, Luther, Nernst, Weigert, Winther, and others.

THE GROTTHUS-DRAPER ABSORPTION LAW.

The fundamental law of photochemistry was discovered in 1817 by Grotthus (Abhandlungen über Elektrizität und Licht, *Ostwald's Klassiker*, Nr. **152,** p. 101). His generalisation was based on theoretical considerations, and was enunciated in the form that " the substance which responds most markedly to a given coloured light shows in its natural state the complementary colour to this light." In other words, since the colour of a substance is due to the non-absorbed light, it is the absorbed light which is effective in initiating chemical change. Not much attention was paid to the work of Grotthus, and a quarter of a century later the same law was re-discovered by Draper, whose name is now most frequently employed in connection with it. Draper (*Phil. Mag.*, [iii], **19,** 195, 1841 ; **23,** 401, 1843 ; **27,** 327, 1845), in an investigation of the photochemical union of hydrogen and chlorine, attributed the enhanced chemical reactivity of chlorine in the light to the radiant energy absorbed by this gas. Expressed in the form that " this quality gained by the chlorine arises from its having absorbed thitonic rays corresponding in refrangibility to the indigo," his views are equivalent to a statement of absorption being the determinative influence in photochemical change. An early example of confirmation of this law was that of Herschel (1842), who showed that the bleaching of the coloured material in flowers is strongest in light complementary to the colour of the flower.

The Grotthus-Draper Law is thus of a purely qualitative character ; it is simply the recognition of the fact that absorption of some part of the light incident on a system is a necessary preliminary to photochemical change in that system. It by no means follows, as we have already seen, that optical absorption is always followed by detectable alteration in the chemical composition of an illuminated system, this being only one of several possible effects of the absorption of light. All material systems absorb some portion of the spectrum, but the photochemical sensitivity of the system may vary from zero to very great values. Thus the element chlorine absorbs violet light, but no permanent chemical change can be detected as a consequence ; addition of small quantities of hydrogen or of carbon monoxide, however, converts the system into an extremely photosensitive one. We are —in general—unable to predict whether a given system will be found to be light-sensitive or not ; our knowledge of molecular excitation, of the properties of activated molecules, and of other relevant matters is at present much too meagre. We know in a qualitative way that compounds of certain elements such as, for example, the halogens, silver, and uranium often show marked sensitivity to light, and the same is true for certain groupings in organic compounds. But many other factors enter, among which may be mentioned the variation from case to case in the sensitiveness of the means used to detect photochemical action, and the effect of the wave-length of the activating light. An excellent example of the latter is afforded by the behaviour of Fehling's solution, which is feebly sensitive to light, the resulting change being the separation of cuprous oxide and the oxidation of tartaric acid. Byk (*Z. physikal. Chem.*, **49,** 680, 1904) showed, however, that reaction does not take place when the illumination employed is the orange portion of the spectrum (absorption of which is the cause of the blue colour of the solution), but that it occurs only when ultra-violet light is used. In this case the orange absorption band is due to copper, the ultra-violet absorption to tartaric acid, and the absorption bands characterising the two components of the system act in different ways. Winther (*Z. wiss. Phot.*, **9,** 229, 1910) cites this case as an example of a generalisation relating to a class of substances for which we may reverse the Grotthus-Draper Law, i.e. for which light-sensitivity may be predicted if they possess selective absorption. He finds in the case of photochemical oxidation-reduction processes that the oxidisable substance is always the light-sensitive constituent, that the sensitivity to light is determined by the absorption capacity of this substance, and that sensitivity to light on the part of the system may be predicted if the oxidisable substance (or group) shows selective absorption. Not much practical significance, however, attaches to these generalisations. While, in so far as oxidation of the oxidisable substance (or group) is equivalent to a loss (or "loosening") of an electron, they constitute an anticipation of modern views, yet when we consider that in such processes as the photochemical interaction of chlorine with hydrogen, carbon monoxide, or hydrocarbons, the chlorine is the light-sensitive constituent and that in ordinary chemical language it is the oxidising, and not the oxidisable constituent, it is seen that no prediction of light-sensitivity on the lines suggested by Winther is practically feasible.

The Grotthus Law does not specify that reaction must be preceded by absorption by one of the reacting species. As we shall see in a later Chapter, many examples of photosensitisation are known, in which the absorbing substance is unchanged chemically, but in which the energy absorbed by it is utilised in activating other substances to reaction.

EINSTEIN'S LAW OF PHOTOCHEMICAL EQUIVALENCE.

Another generalisation of fundamental significance to photochemistry is the Einstein photochemical equivalent law. Introduced in 1912 (Einstein, *Ann. Physik*, [iv.], **37,** 832; **38,** 881, 1912), it is usually stated in a form equivalent to the following: If a photosensitive system is subjected to light of frequency ν, the number N of molecules of the absorbing substance (photolyte) which decompose is equal to $Q/h\nu$, where Q is the radiant energy absorbed, and h is the Planck constant. More simply expressed, for each quantum absorbed one molecule of the absorbing substance disappears. We shall see in the next Chapter that the large number of experimental investigations carried out since 1912 to test the validity of the Einstein relation show that the "law" as above stated is true only in a few cases, but that the evidence for its applying strictly to the primary process in photochemical change is very strong.

The first application of the quantum theory to photochemistry was made in 1905 by Einstein (*Ann. Physik*, [iv.], **17,** 132, 1905), who indicated that if the photochemical reaction were a decomposition of the photolyte into positive and negative ions ($AB \rightarrow B^+ + A^-$) the law should apply. In 1912, he gave a thermodynamic proof of the law for a reaction of the type $XY \rightleftharpoons X + Y$ (see also *Journal de Physique*, **3,** 277, 1912), and in 1916 (*Verh. deut. phys. Ges.*, **18,** 315, 1916) he employed a deduction based on the use of a generalised Bohr atomic model. It should also be mentioned that in the meantime Stark (*Physikal. Z.*, **9,** 889, 894, 1908) had also clearly recognised the importance of the quantum theory in this connection, had derived the photochemical equivalent law, and had advanced modern views on the mechanism of photochemical change. It appears fitting, therefore, to denote this relation as the Stark-Einstein Law.

In his second derivation, Einstein deals (after the manner of Bohr) with a system of identical molecules, each capable of existence in a number of discrete energy states and such that the passage of the molecule from one state to another is accompanied by the absorption or emission of a quantum of radiant energy. Considering two such states of the molecule, the one of lower energy content Z_m is transformed into the one of higher energy content Z_n by absorption of a quantum $h\nu$ of light of frequency ν. The temperature of the system is such that the density of black body radiation of this frequency is almost negligible, so that in the unilluminated system it is to be assumed that practically all the molecules will be in the state Z_m. The further assumptions are made that in addition to the change (1) $Z_n \rightarrow Z_m + h\nu$, molecules in the state Z_n are alternatively capable of undergoing a unimolecular chemical change (2) $Z_n \rightarrow$ Resultants, and that the probability of reaction (2) is great compared with that of (1). If now the system be illuminated by radiation containing the frequency ν, the result will be that each $h\nu$ of radiant energy absorbed will yield one molecule in the Z_n state, and almost every molecule in this state decomposes to yield resultants, i.e. the Einstein Law will be fulfilled. It will be observed that the photochemical process here involves a primary ("light") reaction and a secondary ("dark") reaction, a conclusion previously emphasised by Stark (*loc. cit.*), but not involved in Einstein's thermodynamic deduction of the photo-equivalent relation. Although the latter was first in point of time and certain of the assumptions made in its derivation have exercised a great influence on succeeding work, it does not appear necessary here to reproduce it in full, as the conditions postulated in the thermodynamic proof are such as do not obtain in actual practice. These conditions are as follows. The process studied is the reversible gas reaction

$$XY + \text{Light} \rightleftharpoons X + Y.$$

The primary process is thus assumed identical with the complete reaction and is taken to be a dissociation of the molecule into neutral atoms. The molecules of XY dissociate only by absorption of light, and the frequency interval capable of initiating the reaction is not assumed to be infinitely small. The following additional hypotheses are made:—

1. When the gas XY is exposed to radiation whose frequency is in the neighbourhood of ν, the number of molecules of XY decomposed per unit of time is proportional to the product of the intensity of the radiation (or the radiation density) and the concentration of XY.

2. The energy ϵ absorbed when one gram-molecule decomposes is independent of the intensity of the radiation.

3. The absorption of the energy ϵ of frequency ν is necessarily followed by the decomposition of one gram-molecule of XY. The reverse process *emits* the same amount ϵ of radiant energy of the same frequency ν.

4. The number of molecules of X and Y recombining per unit of time is independent of the radiation density.

5. The energy of the radiation (of frequency ν) emitted per unit of time in the recombination process is independent of the radiation density.

These conditions postulated, Einstein considers the equilibrium which would be established in the gas mixture at a given temperature when the radiation density of frequency ν has a value different from (in general greater than) the black body density at the same temperature. Such an equilibrium, which may be termed a *pseudo-thermodynamic equilibrium*, is of course not practically attainable; it would be ideally possible in a container whose walls were completely reflecting. By an application of the second law of thermodynamics to this equilibrium state, it is possible to derive the photochemical equivalent relation $\epsilon = Nh\nu$, provided that the effective radiation falls within the range of validity of Wien's radiation formula. Einstein states that the same result may be obtained for more complicated gas reactions or reactions in dilute solution, and in his second paper (*Ann. Physik*, **38,** 881, 1912) the theory is extended to the case where the photochemically active light embraces a wide range of frequencies instead of being practically monochromatic. The result obtained is that the total decomposition is the sum of those caused by absorption of the individual frequencies, and that the energy absorbed per molecule decomposed depends simply on the mean frequency of the radiation present and not on any frequency characteristic of the absorbing molecule.

This thermodynamic derivation has been discussed by Weigert (*Z. Physik*, **14,** 383, 1923) and by Allmand (*Trans. Faraday Soc.*, **21,** 438, 1926). The latter finds that " the type of photochemical change for which the Einstein thermodynamic proof rigidly holds is one in which (*a*) all reacting molecules are at the same energy level before reacting and are hence equally reactive; (*b*) the reactivity of the absorbing molecules under a given radiation density is independent of temperature; (*c*) the amount of energy absorbed per absorbing molecule is the same in every case and is independent of temperature; (*d*) the product after the absorption of energy is fundamentally unstable with respect to the original absorbing system, and will revert to the latter spontaneously at a rate independent of temperature. The whole process is identical for all the molecules."

As pointed out by Allmand, all these conditions are fulfilled for the primary " light " action adopted by Einstein in his second derivation, viz. the passage of an electron to a higher quantum orbit according to $Z_m + h\nu \rightarrow Z_n$. We may conclude therefore that, so far as is known at present, the only process for which the Stark-Einstein Law can be thermodynamically proven is the activation of a generalised Bohr model and that no known photochemical reaction actually fulfils *a priori* the conditions necessary for the Einstein proof to hold.

Actual photochemical reactions in all cases involve a primary " light " process followed by secondary processes which are thermal reactions and whose velocity constants are independent of light intensity. The photochemical yield thus becomes very dependent on the nature and extent of the secondary processes, and the Einstein Law, though holding for the primary process, need not hold for the net reaction. In spite of this, the application of the quantum theory by Einstein has had important consequences, among which the most material is the aid which it gives to investigation of the mechanism of photochemical reaction. We shall defer further consideration of the photochemical equivalent law until the next Chapter.

TYPICAL EXAMPLES OF PHOTOCHEMICAL ACTION.

As already mentioned, all types of chemical change may be brought about under the influence of light. For various reasons, however, certain types of reaction and reactions involving certain elements have received much more attention than others. Most photochemical investigations have been carried out with light limited to a range of wave-lengths between 600 and 200 $\mu\mu$, and thus the photoactive constituent of the system must necessarily absorb in this spectral region. Very characteristic absorption bands in the visible spectrum are possessed by the halogens, so that attention was early paid to the photochemical reactions involving these elements. Since also many of these reactions are of great interest and have presented certain baffling features, it is not surprising that a large number of workers have been attracted to this field. Specially prominent in this connection is the photochemical reactivity of chlorine. Very characteristic reactions of this element are its combination with hydrogen, with carbon monoxide, and with sulphur dioxide, the photo-decomposition of chlorine water, and substitution reactions with such organic substances as toluene and trichlorobromomethane. Of great importance theoretically are also the gas reactions in which chlorine acts as a sensitiser

(Weigert, *Ann. Physik*, **24,** 252, 1907). These include the decomposition of ozone, the union of hydrogen and oxygen, and the formation of sulphur trioxide from sulphur dioxide and oxygen. Though not so markedly as that of chlorine, the photochemistry of bromine and of iodine has also received considerable attention. Important reactions involving the first-named element are its union with hydrogen and certain reactions in which it acts as a sensitiser, viz. the decomposition of ozone, the transformation of the ethyl ester of maleic acid to ethyl fumarate in CCl_4 solution, and the reaction between dissolved oxygen and CCl_3Br (in CCl_4). Of iodine reactions, mention may here be made of the photochemical reaction between iodine and potassium oxalate in aqueous solution, and the photosensitising action of the I_3' ion on the oxidation of aqueous HI.

The photochemical decompositions into their elements of gaseous HI and HBr are also noteworthy processes; the former reaction was the first photochemical process to be studied from the standpoint of the determination of reaction "order" (Bodenstein, *Z. physikal. Chem.*, **22,** 23, 1897), and both reactions are of exceptional interest from a theoretical point of view.

Of the other non-metallic elements, the most prominent in the literature is probably oxygen. This is partly due to the fact that many insolations have been conducted with the insolated material in contact with atmospheric oxygen, so that photochemical oxidations were among the first reactions to be noted and studied. Further, on illumination by short wave ultra-violet light, elementary oxygen is itself converted into its allotrope ozone, and this process as well as the photochemical reactions of ozone possess a considerable degree of interest.

Among metallic compounds, those of silver have received abnormal attention, owing, of course, to their importance in photography. The basic photochemical processes here involved are the decompositions of the halides AgCl, AgBr, and AgI, and these reactions form almost the only well-investigated cases of photochemical reactions in solids. Of the other metallic compounds, the most studied cases are to be found in those relating to compounds of mercury, chromium, iron, cobalt, and uranium (uranyl salts).

In the domain of organic chemistry, qualitative data for many reactions have been obtained, but, owing to the complicated nature of most of these, fewer quantitative investigations of the kinetics and quantum yields have been carried out than for inorganic reactions. Much of our knowledge of organic photochemical processes we owe to the researches of Ciamician and Silber,* and of D. Berthelot and Gaudechon (*Compt. rend.*, 1910-1913). Typical examples of such processes are the following:—

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* See, for example, Ciamician (*Bull. Soc. chim.*, June, 1908) and Paterno, *Light Syntheses in Organic Chemistry*; Rome, "Tipografia Editrice Italia," 1914.

Photolyses and Decompositions.—Specially characteristic are the decompositions of aldehydes, ketones, and acids in ultra-violet light, studied by Berthelot and Gaudechon. Many of these reactions are, however, of a complex nature and yield a mixture of products. Thus formic acid in aqueous solution is decomposed by ultra-violet light in two ways, (α) $H.COOH \rightarrow CO_2 + H_2$, (β) $H.COOH \rightarrow CO + H_2O$; and in addition, secondary processes resulting in the formation of formaldehyde and other products occur. Acetaldehyde undergoes both photolysis and polymerisation on exposure to ultra-violet light—

$$(a)\ CH_3.CHO \rightarrow CH_4 + CO,$$
$$(b)\ 3CH_3.CHO \rightarrow \text{paraldehyde, etc.}$$

Acetone is decomposed according to

$$CH_3.CO.CH_3 \rightarrow CO + C_2H_6.$$

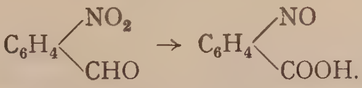
Hydrolyses.—Of the simpler reactions in this category, mention may be made of the hydrolysis of monobromo- and monochloro-acetic acids in aqueous solution—

$$CH_2X.COOH + H_2O \rightarrow CH_2(OH).COOH + HX,$$

and of the characteristic reaction between acetone and water—

$$CH_3.CO.CH_3 + H_2O \rightarrow CH_4 + CH_3.COOH.$$

Molecular Rearrangements.—Stereoisomeric changes in organic compounds brought about by the action of light are not uncommon. One of the simplest and best investigated cases is the reversible transformation between maleic and fumaric acids, both reactions being sensitive to ultra-violet light. Other types of intramolecular photochemical change are met with, for example, in nitro compounds. Thus, in benzene or acetone solution, *ortho*-nitrobenzaldehyde is converted under the influence of violet light into *ortho*-nitrosobenzoic acid



$$C_6H_4\begin{cases}NO_2\\CHO\end{cases} \rightarrow C_6H_4\begin{cases}NO\\COOH.\end{cases}$$

In this category also fall the so-called *phototropic* changes. This was the term used by Marckwald (*Z. physikal. Chem.*, **30,** 140, 1899) to denote the change of colour suffered by certain solid organic substances on illumination; in the dark, or more rapidly on heating, the original colour is restored. Phototropy was first discovered in tetrachloro-α-keto-naphthalene, a white substance which reddens on illumination. A large family of phototropic substances was discovered by Stobbe (*Z. Elektrochem.*, **14,** 482, 1908) and termed by him fulgides. They are derivatives of butadienedicarboxylic acid and its anhydride.

Polymerisations.—Many unsaturated organic compounds have a tendency to polymerise, in some cases in the dark, but more often on illumination with light of suitable wave-length. Two types of condensation may be distinguished according as to whether or not the reverse depolymerisation takes place spontaneously (or on heating). Examples of the reversible type are the photochemical polymerisation of anthracene and of methylanthracene. In both cases a dimeride results which tends spontaneously to depolymerise. Of the irreversible type, typical cases are the polymerisation of the halides of unsaturated aliphatic hydrocarbons, for example, vinyl bromide $CH_2 = CHBr$, which in ultra-violet light rapidly polymerises to a solid of high molecular weight and unknown constitution.

Oxidations.—Photochemical oxidations are, as mentioned above, numerous. Two kinds may be differentiated, (*a*) those in which the oxidation is effected by atmospheric oxygen, (*b*) those in which an oxidising agent is present in the system. A well-investigated but rather complex case of the latter is the photochemical oxidation of quinine by chromic acid (Luther and Forbes, *J. Amer. Chem. Soc.*, **31,** 770, 1909). In the former class, the oxidation may occur *via* the formation of ozone due to absorption of radiation by the oxygen, but in the large majority of cases it is probable that the other reactant is the substance which absorbs and is then oxidised. Most of these reactions have been subjected only to examination of a qualitative nature, and in many cases complex products of unknown constitution are formed. Among the ones more quantitatively studied is the photochemical oxidation of the leuco bases of the triphenylmethane series to the corresponding dyes (Gros, *Z. physikal. Chem.*, **37,** 157, 1901). Finally, we have organic *syntheses*, the most important of which is the naturally occurring photosynthesis of carbohydrates from CO_2 and H_2O—

$$mCO_2 + nH_2O \rightarrow C_mH_{2n}O_n + mO_2,$$

the process occurring in plants in the presence of the photosensitiser, chlorophyll.

DEFINITIONS.

Light-Sensitivity.—We may define the sensitivity to light of a system as the extent of chemical change (expressed in gram-molecules of reactants disappearing or of resultants formed) per unit of light energy absorbed. The sensitivity thus obtained may vary over a very wide range, from cases in which reaction can only be detected by using strong illumination over long periods of time, to cases such as the hydrogen-chlorine reaction which, when the gases are pure, is remarkably light-sensitive.

The possibility of photochemical action depends in certain cases on the presence of suitable *acceptors* in the illuminated system. The term is used to denote the substance which reacts with the product formed as a result of the primary " light " reaction. Thus, illumination of bromine by violet or blue light, which is strongly absorbed, causes no chemical change, so far as we are able to detect. Addition of hexahydrobenzene C_6H_{12}, which acts as an acceptor for the resultants of the action of light on bromine, leads to a photochemical reaction, the formation of the bromo-compound and HBr. The nature of the acceptor for a given activated molecule may have a great influence on the photosensitivity of the resulting system and on the characteristics of the photochemical process which takes place. Thus hydrogen, carbon monoxide, and trichlorobromomethane (CCl_3Br) are all acceptors for chlorine photochemically activated, but there are very marked differences between the three reactions which ensue. It is not necessary to postulate that the acceptor molecules must be of a different molecular species from those with which they react. To take an example, a possible mechanism for the photochemical decomposition of ammonia into its elements is a reaction between activated and non-activated NH_3 molecules. The latter may then be regarded as acceptors.†

The terms *catalyst* and *negative catalyst* (*inhibitor*) have much the same significance applied to photochemical processes as to thermal reactions. They are substances which exert respectively a positive and a negative effect on the reaction velocity, without themselves appearing in the stoichiometric equation connecting reactants and resultants. Very frequently (but not necessarily) small quantities exert a powerful accelerating or retarding effect on the reaction rate. In the case of photochemical reactions a further condition to be satisfied by both catalysts and inhibitors is that they do not appreciably absorb the effective radiation.

Photosensitisation is said to occur when the effective radiation is absorbed, not by one of the reactants, but by a *photosensitiser*, which itself suffers no permanent alteration. The energy absorbed by molecules of the latter is thus transferred in some way to reactant molecules, which are thereby stimulated to reaction. The most frequently occurring examples are those in which absorption of radiation of long wave-length by the photosensitiser induces photosensitivity in a system which otherwise would respond only to light of shorter wave-length. A familiar example of such photosensitisation is the light-sensitivity of panchromatic plates. The addition of certain dyes which absorb in the yellow and red renders the silver bromide, which itself absorbs only shorter wave-lengths, sensitive to the longer wave light. Photosensitised gaseous reactions are of great theoretical importance; they are possibly the simplest types of photochemical change. Characteristic examples are the decomposition of ozone sensitised by chlorine or bromine and the dissociation of H_2 sensitised by mercury vapour. When the photosensitisation is effected by a product of the " light " or of a " dark " reaction, *autosensitisation* is said to take place. Examples are (1) the photochemical oxidation of HI in aqueous solution by dissolved oxygen, in which the sensitiser is I_3' first produced by a " dark " reaction, and (2) the photochemical oxidation of leuco bases of the triphenylmethane series.

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† Allmand (*Chem. Soc. Ann. Reports*, 1925, p. 363) extends the definition of an acceptor to include all cases in which chemical reaction follows a collision of an activated molecule with a non-activated one. The reactions which may occur as a result of collision between an activated molecule A^* and an ordinary molecule B may be written:

(*a*) $A^* + B \rightarrow$ Resultants; (*b*) $A^* \rightarrow$ Resultants; (*c*) $B \rightarrow$ Resultants.

While the choice of the word acceptor is perhaps not very fortunate, we should prefer to limit its application to the cases in which reactions of type (*a*) result from the collision. Case (*c*) is better regarded as an example of photosensitisation and (*b*) may be termed "catalysis."

Retardation of a photochemical reaction as a result of one of the non-reacting components of the system absorbing some of the effective radiation is sometimes termed *negative photosensitisation*. In several such cases, one of the reaction products acts as a retarder in this way, and thus the negative effect increases as the reaction progresses. An example is encountered in the photochemical decomposition of HI; if the reaction is allowed to proceed to an appreciable extent or if I_2 is added initially, the reaction is retarded owing to the diminished energy available for the HI.

Photochemical Induction.—This was the name given by Roscoe and Bunsen to a phenomenon previously discovered, but first closely investigated by them, in the case of the photochemical union of hydrogen and chlorine. The *induction period* is the time required after the start of illumination for the reaction to proceed with its maximum velocity. Induction periods are also found in certain thermal reactions, but they are more frequent and striking in photochemical processes. They are due in the latter case mainly to the presence of small quantities of impurities which act as negative catalysts and whose destruction is the chief process which occurs during the period of induction. Sometimes they are due to autosensitisation of the measured process by a product of an accompanying " dark " reaction. Induction periods are, however, no more characteristic of photochemical reactions than they are of thermal reactions. In the latter, they may be obtained whenever the total process occurs in a series of intermediate stages whose velocities are not too different, and also they may appear as a consequence of autocatalysis or of secondary processes which prevent the normal course of the reaction.

Photochemical Extinction.—Bunsen and Roscoe, in the course of their work on the photochemical union of hydrogen and chlorine, interpreted certain of their experiments as showing the existence of two kinds of extinction, optical extinction and photochemical extinction. According to these investigators, the former is the energy absorbed by chlorine when alone, and is utilised solely in raising the temperature; the latter is the *additional* absorption when hydrogen is added, and is attributed to the energy required for the initiation of chemical reaction. Photochemical extinction is thus the alleged excess absorption when a photochemical reaction is occurring, over and above that calculated from the concentration of the absorbing constituent. Later work has, however, failed to confirm the existence of a photochemical extinction. In a very careful re-investigation of the hydrogen-chlorine reaction by Burgess and Chapman (*J.C.S.*, **89,** 1430, 1906), a direct comparison of the light absorbed by a mixture of chlorine and hydrogen with that absorbed by a mixture of the same quantity of chlorine with an inert gas (air) was made. The result obtained was that the two absorptions were—within the narrow limits of experimental error—identical, and thus no extra absorption is required for the process of combination. The same identity has been proven for the chlorine-sensitised decomposition of ozone (Weigert, *Z. Elektrochem.*, **14,** 591, 1908), and for the photo-reaction in Eder's solution

$$2HgCl_2 + (NH_4)_2C_2O_4 \rightarrow Hg_2Cl_2 + 2CO_2 + 2NH_4Cl$$

by Winther (*Z. wiss. Phot.*, **8,** 237, 1910). All these reactions are accompanied by a decrease of free energy, the light acting as a "catalyst," but there is no reason to suppose—on the basis of modern views—even when the system gains free energy as a result of the photochemical reaction, that any sensible increase in absorption takes place. From the standpoint of the quantum theory, it is clear that no extra absorption is necessary: the primary process of quantum absorption yields activated molecules, which under suitable conditions may react to yield the reaction products or may lose their quantised energy by dissipation into thermal energy.

CLASSIFICATIONS OF PHOTOCHEMICAL REACTIONS.

No satisfactory classification of photochemical processes appears possible at present. From the standpoint of the quantum theory, the primary action of light is the activation of the absorbing atom or molecule; this may be followed by a variety of secondary processes (both chemical and physical) the nature and extent of which may be markedly dependent on the experimental conditions. Our knowledge of the nature of these processes is, however, insufficient to enable a classification based on reaction mechanism to be made—even if such a classification is a feasible one—and therefore we must be content with other modes of grouping of photochemical processes which are more or less formal and which are of a less fundamental character.

The first classification of photochemical reactions to be attempted was that based on the energy changes accompanying the process. Two categories of reactions thus occur, (α) reactions in which the end state has a greater free energy than the initial state, and (β) reactions accompanied by a decrease in free energy. This classification was originally suggested by Helmholtz* (1847), and was adopted by Warburg (*Verh. deut. phys. Ges.*, **9,** 753, 1907), by Winther (*Z. wiss. Phot.*, **9**, 229, 1911), and in especial by Weigert (*Z. wiss. Phot.*, **10,** 1, 1911). In reactions accompanied by a gain in free energy, the light acts against the chemical forces of the system, the absorbed radiant energy is converted (partially) into free chemical energy, and there will therefore be a tendency for the resultants of the process to revert spontaneously into the reactants. If the latter (dark) reaction is sufficiently rapid, there will eventually result a photostationary state, in which the photochemical direct reaction is exactly balanced by the spontaneous reverse process. This photostationary state is to be distinguished from a " thermal " chemical equilibrium as it does not obey the law of mass action. It is maintained solely at the expense of the light energy entering and absorbed by the system, and if the source of light be removed the system reverts to its original state. In the case of photochemical reactions involving a diminution in free energy, the light acts as a catalyst in initiating or hastening a reaction which yields the equilibrium state under the given conditions of temperature and pressure, but whose velocity is usually (but not always) inappreciable in the absence of light. In these " catalytic " light reactions, the function of the absorbed radiant energy is to lessen the " chemical resistance " of the system so that the reaction accompanied by a decrease in free energy may take place. Typical examples of reactions in which there is a gain of free energy are the polymerisation of anthracene to dianthracene, the ozonisation of oxygen in ultra-violet light, and the naturally occurring photosynthesis in which carbon dioxide and water are converted into starch and oxygen under the action of sunlight. The first and second of these processes are reversible, and under suitable conditions yield photostationary states. The third reaction, which is accompanied by a large gain in free energy,* requires the presence of chlorophyll for its consummation. It evidently has a complex mechanism and is not reversible in the same sense as the other two examples of " energy-storing " processes given. The most familiar example of a " catalytic " photochemical process is the much studied union of hydrogen and chlorine. The equilibrium conditions of the system are such that at ordinary temperatures no detectable quantities of reactants (assuming them brought together in equivalent proportions) exist. The reaction is strongly exothermic and is accompanied by a large decrease in free energy. In the dark a mixture of hydrogen and chlorine is quite stable (really metastable), in diffuse light the two gases combine slowly, while in strong light combination occurs with explosive violence. The action of light in this case has been likened to that of a trigger, or to " the match which lights a bundle of firewood " ; it is evident that in this reaction and in others of a similar type we have the possibility of a small amount of light energy initiating a large amount of chemical change.

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* H. v. Helmholtz, "Uber die Erhaltung der Kraft," (*Ostwald's Klassiker*, No. 1).

Convenient as is this classification in certain respects, it suffers from the drawback that it tends unduly to emphasise the total change and not sufficiently the photochemical part of the process. It has long been recognised, and in particular emphasised by Ostwald (*Lehrb. d.*

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* The gain in *total* energy of the system per gram-molecule of CO_2 transformed is the heat of combustion of 27 grams of starch or 113,000 cal.

Allg. Chem., II. (1), 1087) and by Weigert (*Ahrens Sammlung*, **17**, 190, 1912), that in all photochemical reactions the true photochemical process, the primary process, is attended by an increase in free energy of the system. In all cases there is work performed by light on the system, and the absorbing substance is converted into a modification with higher energy content. The primary products of the "light" reaction may react further with evolution of heat, but this is quite secondary and is not essential to the primary action of the radiant energy. The analogy employed by Ostwald (*loc. cit.*) is perhaps helpful in this connection. A rectangular block (parallelopiped) resting on its base is in a position of equilibrium, for after a slight displacement it returns to its original position. If, however, the displacement is sufficiently great, the block will fall on its side, i.e. to a second equilibrium state. The energy of the system may be decreased or increased according as the centre of gravity is lower or higher in the second position, but in both cases a preliminary expenditure of work is necessary to cause the change from the initial to the labile state (when the block is on its edge). The former case corresponds to a "catalytic" light reaction, the latter to an "energy-storing" process, but, whether the total energy change be positive or negative, the essentially photochemical part of the process is always associated with an increase of energy in the system.

Further, as has been pointed out by Weigert (*loc. cit.*), the classification cannot be applied in many cases owing to lack of the necessary energy data. This is particularly the case for organic reactions, where very often the differences between the heats of combustion of reactants and resultants are so small that we are left in doubt as to whether a free energy increase or decrease is associated with a given reaction.

Before discussing other classifications, it will be convenient to make brief mention now of attempts which have been made to apply classical thermodynamics to photochemical reactions, although admittedly such considerations have exerted practically no influence on the development of photochemistry. The study of "light" reactions is very intimately connected with the subject of chemical kinetics, and although thermodynamics will predict which chemical processes ("dark" reactions) are possible, it gives no information as regards whether or not they actually will occur, or, if they do occur, with what velocity. Again, though in photochemical work equilibrium states are often encountered, they are not amenable to thermodynamic treatment owing to the fact that the systems under investigation are not homogeneous either with respect to radiation density or to concentrations of reacting substances. Owing to absorption of light, there will be a decrease in radiation density of the effective wavelength in the direction in which light penetrates into the system, and this, as a necessary consequence, will entail concentration gradients in the system. Diffusion processes will thus set in, the system then behaving as if it possessed different temperatures at different places, with the result that it becomes impossible to apply the second law of thermodynamics. Again, the photostationary state can only be maintained by the continuous expenditure of light energy, and the absorption of light is thus necessarily bound up with an irreversible conversion of radiation into heat. Trautz (*Z. wiss. Phot.*, **4,** 351, 1906; **6,** 169, 331, 1908) and Nernst (*Z. Elektrochem*, **13,** 550, 1907) considered that if the reacting substance were present in a sufficiently thin layer, the system might then be considered homogeneous with respect to light and material, and thermodynamical considerations might be applied. This has been attempted by Trautz (*loc. cit.*), who dealt with photostationary states and with the influence of temperature on photochemical reactions, but without obtaining any results of general validity.

E. Warburg (*Ber. deut. phys. Ges.*, **9,** 753, 1907; *ibid.*, **11,** 654, 1909) and Trautz (*loc. cit.*) have considered photostationary states from the point of view of the difference between the temperature of the system and that of the light source. For reactions accompanied by an increase in free energy, the displacement of the equilibrium state caused by light will naturally be in the same direction as that produced by elevation of temperature. Assuming the light source to be a black body, it is found that the maximum possible transformation of radiant energy into free energy A of the system is given by

$$\frac{A}{Q}=\frac{T_\nu - T}{T_\nu},$$

where T_ν = temperature of the radiation, T = temperature of the system, and Q is the energy absorbed. Since, in general, the activating light in photochemical reactions lies in the blue, violet, or ultra-violet, the intensity of which does not become appreciable in black body radiation until very high temperatures are reached, T_ν is much greater than T, and the fraction of the absorbed energy which may be utilised for chemical work is practically unity. Byk (*Z. physikal. Chem.*, **62,** 454, 1908) and Weigert (*ibid.*, **63,** 454, 1908) have applied thermodynamic considerations to the photochemical conversion of anthracene into dianthracene, a reaction which was investigated in detail by Luther and Weigert (*Z. physikal. Chem.*, **51,** 297, 1905; **53,** 385, 1905). They indicate the possibility of calculating the upper limit for the velocity of this "energy-storing" process which eventually leads to a photostationary state.

None of these general applications of thermodynamics to photochemistry have, however, been of any great service; much more helpful is the application in specific cases to the consideration of reaction mechanism. Thermodynamics may then be applied to decide, on the basis of an assumed mechanism for a primary photochemical process, what secondary reactions are possible. Examples of such a treatment are given in the next Chapter; they constitute according to Nernst and Noddack (*Sitzungsber. Preuss. Akad. Berlin*, p. 110, 1923) the only legitimate applications of classical thermodynamics to photochemical processes.

Another classification of photochemical reactions, one based on Einstein's photochemical equivalent law, was recommended by Bodenstein (*Z. physikal. Chem.*, **85,** 333, 1913). He terms "primary light reactions"[*] those in which the number of molecules disappearing in the total reaction is approximately equal to (or exceeds by a small multiple) the number of quanta absorbed. They are also characterised by (*a*) proportionality between reaction velocity and absorbed radiation, (*b*) a temperature coefficient of unity, (*c*) no influence of foreign substances on the reaction rate except in so far as these bodies absorb the active light. As examples of such reactions were given—among others—the decomposition of HI, the ozonisation of oxygen, and the polymerisation of anthracene. "Secondary light reactions," according to Bodenstein, are those in which the photochemical yield is much greater (or less) than that predicted by application of Einstein's Law. Reactions cited as examples of such were the combination of hydrogen and chlorine, the decomposition of ozone, the decomposition of hydrogen peroxide, and the oxidation of HI. This classification presents this in common with the older thermodynamic classification, that it groups together as possessing high quantum yields many of the same reactions as were previously grouped together as exothermic. A weakness of the classification is that it does not distinguish between reactions with low quantum yield and those with high; in its favour is the recognition that the velocities of certain photochemical processes (of which the decomposition of HI or of HBr is the best example) are practically independent of all other factors except the absorbed energy, such processes having in all probability very simple mechanisms which function over large ranges of temperature, pressure, etc. Yet no satisfactory classification of photochemical reactions on the basis of quantum yield alone is possible, as will be seen on consideration of the factors which influence this quantity (cf. Chapters VIII. and IX.).

A quite different scheme has been adopted by Noddack (*Handbuch der Physik*, Vol. XXIII., p. 594: Berlin (Springer), 1926). His classification—which is purely formal—is based on the change in the number of molecules as a result of reaction. He distinguishes four types of process: (1) transpositions or rearrangements in the same molecule, e.g. $AB \rightarrow BA$; (2) photolyses or decompositions with *increase* in the number of molecules, e.g. $AB \rightarrow A + B$; (3) syntheses with *diminution* in the number of molecules, e.g. $A + B \rightarrow AB$; (4) double decompositions with no alteration in the number of molecules, e.g. $AB + CD \rightarrow AD + BC$. No considerations of reaction mechanism or of order of reaction are involved in this system, which is based only on the difference between initial and final states. The adoption, if required, of a purely formal scheme of such a type as Noddack's seems to be the best that can be done in the way of classification of photoprocesses at the present state of our knowledge.*

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[*] The use of the word "primary" in this connection is open to the objection that it may lead to confusion with the usually accepted significance and the one used in this book, viz. the primary reaction is the initial result of light absorption.

METHODS OF EXPERIMENTAL INVESTIGATION.

A brief account of the methods which have been employed in photochemical work may now be given. We shall deal with the subject only in broadest outline and refer the reader to the papers cited in the next Chapter for experimental details.†

Light Sources.—The chief desideratum in a source of light for photochemical work is that its intensity should remain constant during the time required for an experiment or preferably for a series of experiments. It is also usually necessary to employ a light of strong intensity, in order to obtain a conveniently measurable yield of product in a reasonable time. The chief sources which are employed are mercury vapour lamps, with or without the addition of other metals such as zinc and cadmium (amalgam lamps), the carbon arc, metal arcs or sparks, and metal filament lamps. The carbon arc may be made to yield a very intense light, but in general it is not very suitable for photochemical work, as it is difficult to maintain the intensity of its emission sufficiently constant. The most used source of light is the mercury vapour lamp, which gives a rich line spectrum extending from the infra-red into the ultra-violet, the most intense lines being found at 579-568 $\mu\mu$, 546 $\mu\mu$, 435 $\mu\mu$, 405 $\mu\mu$, 365 $\mu\mu$, 313 $\mu\mu$, and 254 $\mu\mu$. Additional lines may be introduced by the employment of amalgams containing zinc, cadmium, or thallium. Mercury vapour lamps are constructed either of "uviol" glass, which transmits wave-lengths longer than 254 $\mu\mu$, or of quartz.‡

For photochemical work in the region 190-240 $\mu\mu$, the light emitted by the quartz mercury lamp is too weak, and it must be replaced by metal "spark" spectra. Such have been extensively used by Warburg (*Z. Elektrochem.*, **27**, 133, 1921; cf. also *Sitzungsber. Preuss. Akad. Berlin*, p. 216, 1912); using zinc electrodes, groups of lines near 207 $\mu\mu$ and 253 $\mu\mu$ were isolated and employed; with magnesium electrodes, a group round 282 $\mu\mu$. The conditions necessary for the maintenance of constant intensity were investigated, and it was found possible to limit the deviations from the mean intensity—over the time required for an experiment—to about six per cent. Metal filament lamps may be used as a source of visible light when strong intensity is required for wave-lengths not emitted by the mercury vapour lamp. Very little work has been done using infra-red radiation as the source of activation; in two recent attempts by H. A. Taylor (*J. Amer. Chem. Soc.*, **48**, 577, 1926) and Daniels (*ibid.*, **48**, 607, 1926) to decompose N_2O_5 by infra-red light, the carbon arc and the Nernst glower were employed.

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* Other classifications of photochemical reactions have been proposed by Schidlof (cf. *Chem. Soc. Abstracts*, **106**, (2), 601, 1914), and Plotnikow (*Lehrbuch der Photochemie*. Berlin and Leipzig (de Gruyter & Co.), 1920). The former groups photochemical reactions according to the direction in which the equilibrium state is displaced by altering the frequency of the activating light. Plotnikow attempts a classification based on the temperature coefficients of photo-processes. He believes that three groups of reactions can be distinguished, with temperature coefficients of about 1·0, 1·2, and 1·4 respectively. There is, however, no warrant from either the theoretical or the experimental side for such a division (cf. Chapter XII.).

† Particularly the papers of Warburg (*Sitzungsber. Preuss. Akad. Berlin*, 1911-1919), and also the critical summary of Forbes (*J. Physical Chem.*, **32**, 482, 1928).

‡ The factors which have to be considered in the use of the quartz mercury arc as a light source for quantitative photochemical work have recently been investigated by Reeve and his collaborators (*J. Physical Chem.*, **29**, 39, 713, 1925; **30**, 1427, 1926). They emphasise the fact that individual lamps vary in their characteristics, and give data showing how the total radiation and the intensities of various portions of the spectrum depend on factors such as the voltage, the degree of cooling, the extent of absorption by mercury vapour ("self-absorption"), and the discoloration of the quartz by ageing.

Monochromatism.—A thorough investigation of any photochemical reaction requires the determination of the sensitivity of the system to light of different frequencies, and recent work, stimulated by the appearance of the Einstein Law, has concentrated to a considerable extent on this branch of the subject. As the photochemical yield per unit of absorbed energy varies in general with the wave-length, and as also the absorption of the photolyte may vary markedly with wave-length, it is clear that such work requires the employment of light as monochromatic as is consistent with other considerations. Since high intensity is also desirable a compromise must be made, which in most cases has been in the direction of sacrificing purity of light in favour of intensity. A reasonable degree of monochromatism (wave-lengths comprised within a range of say 10 $\mu\mu$) would seem to be all that is required for most photochemical work, though the work of Kuhn on the photo-decomposition of ammonia (p. 468) indicates that further investigation of photo-reactions with increased purity of activating light may be necessary.

Two methods have been employed to obtain light confined to within small limits of wave-length—spectral decomposition of the light and the use of light filters. The former method is not, as a rule, feasible except with a line source. With a continuous source, a narrow spectrometer slit is required to obtain a pure spectrum, and the intensity of a given small portion of the spectrum is, in general, too feeble for photochemical purposes. With spark spectra and with mercury vapour lamps, the method is the best available and it has been used by Warburg, by Kuhn, and by Villars (*J. Amer. Chem. Soc.*, **49**, 326, 1927). The last-mentioned author has described the construction of a monochromator suitable for work with ultra-violet light. The employment of light filters (solid, liquid, or gaseous) is the more usual method of isolating a limited spectral region, though the transmission bands so obtained are often somewhat broad. Combinations of various substances are usually employed in photochemical work; many such are described in the literature. Suitable filters for use with the mercury vapour lamp have been described by Eggert and

Noddack (*Z. Physik*, **20,** 299, 1924). For the isolation of the 2537 Å line of the mercury arc, the Oldenburg filter (*Z. Physik*, **29,** 328, 1924)—chlorine under a pressure of 6·5 atm.—is useful. Chlorine-bromine filters for the same purpose have been described by Peskoff (*Z. wiss. Phot.*, **19,** 10, 1919) and by Anderson and Robinson (*J. Amer. Chem. Soc.*, **47,** 718, 1925). Convenient filters for general and qualitative work are the gelatine films, impregnated with dyes, supplied by Messrs. Kodak Ltd. and others.

Measurement of Light Intensity and Absorption.—A complete study of a photochemical reaction necessitates measurements of absolute values of the absorbed radiant energy. This may be effected either by measuring the incident energy and determining the absorption by optical or other methods, or by determination of two absolute amounts of energy—before and after absorption. For estimation of light energy in absolute units, methods which depend on the total transformation of the energy into heat are employed ; in photochemical work the instrument almost invariably used is either the thermopile or bolometer. Details of the construction and use of these instruments are given by Coblentz (*J. Optical Soc. Amer.*, **7,** 439, 1923), Weigert (*Optische Methoden der Chemie*, Leipzig, 1927), and Jung (Chapter in *Handbuch der Arbeitsmethoden in der Anorganischen Chemie*, Berlin and Leipzig, 1925). In most quantitative photochemical work hitherto done, the Hefner amyl acetate lamp has been used as the radiation standard for calibrating thermopiles and bolometers ; most values of quantum yields of photo-processes are thus dependent on the value ascribed to the energy emitted by this standard. In the majority of cases, the value obtained by Gerlach (*Physikal. Z.*, **21** 299, 1920) appears to have been employed. Measurements of absorption coefficients also lie outside the scope of this book ; references to the literature and descriptions of methods most in present-day use will be found in Weigert's book (mentioned above) and in a paper by de Laszlo (*J. Physical Chem.*, **32,** 503, 1928). Here, attention may briefly be drawn to a few points. It is often of interest to determine whether Beer's Law holds for the absorbing substance ; if the latter is a reactant and if absorption is of moderate magnitude, treatment of reaction kinetics requires this information. The absorption coefficient of a substance in liquid solution or even in the gaseous state can be altered by the addition of non-absorbing substances to the system. Further, in cases where absorption by solvent or by reaction product is appreciable, this should be determined and correction applied for it.* Allowance must also be made in absorp-

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* If two substances which both obey Beer's Law and which do not influence each other's absorption are present at concentrations c_1 and c_2, the total absorption in a thickness x is given by

$$A = I_0\{1 - e^{-(i_1c_1 + i_2c_2)x}\},$$

in which i_1 and i_2 are the absorption coefficients of the two substances. The absorption of the first substance is

$$A_1 = \frac{i_1c_1}{i_1c_1 + i_2c_2} . A.$$

tion measurements for losses due to reflexion at quartz or glass surfaces (cf. von Halban and Ebert, *Z. physikal. Chem.*, **112,** 335, 1924). Errors of from 10 per cent. to 20 per cent. in the measurement of light quantities are not uncommon in photochemical work; a considerable part of the error is, however, due to inconstancy of light source.

Methods of Varying the Light Intensity.—In order to change the intensity of light (incident on a reaction vessel) without change of spectral distribution of energy, various methods have been used. They include the following: variation of distance between source and reaction vessel; use of crossed Nicols; employment of wire screens; change in slit width (using monochromatic light); use of rotating sectors (see p. 407).

Reaction Vessel.—Temperature control is usually not so important as in the determination of thermal reaction velocity. Cases of high temperature coefficients are, however, not unknown in photochemical reactions, and it is usually advisable to have some means of controlling the temperature. Thus, for work at ordinary temperatures, water jacketing may be used or alternatively jacketing by the use of the solution used as a light filter. Reaction vessels may be of various types, but the disposition of the light with respect to the insolated system is of importance. For quantitative work, it is best to use a parallel beam of light, of equal intensity at all points in the cross-section, and travelling at right angles to the plane-parallel sides of quartz or of glass of the reaction vessel. With a point source, a parallel beam may be obtained with a suitable lens system; for other light sources, a small portion of the emitting surface may be isolated and used as source. It is usually unnecessary for the whole of the reaction vessel to be in the path of the beam; the volume of reaction mixture and the cross-section of the beam should, however, be known. For processes in which the absorption of light is great it is advantageous to employ stirring of the reaction mixture, especially if the reaction is a rapid one occurring in a liquid medium.

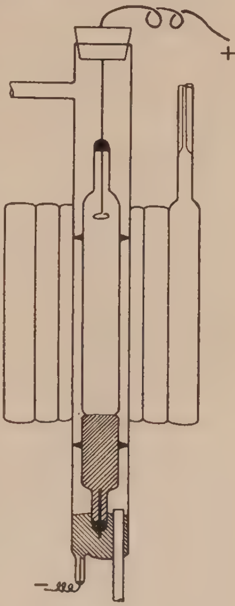

FIG. 43.

In order to obtain the maximum possible utilisation of the radiation of the source of light, reaction vessels of quartz have been constructed with the mercury arc inside. Such for example, are described by Coehn and Becker (*Z. physikal. Chem.*, **70,** 88, 1919) and by Marshall (*J. Physical Chem.*, **30,** 34, 1926). Marshall's apparatus is illustrated by Fig. 43. The innermost compartment contains the lamp, with a mercury cathode and tungsten spiral anode, which is cooled by water circulating upwards. Concentric with the water jacket lie (1) an evacuated compartment which allows the temperature of the reaction vessel to be controlled independently of that of the lamp, (2) a compartment which may be used to contain light filters, and (3) the reaction vessel (outermost tube). The whole apparatus may be immersed in a thermostat. In a later paper (*J. Physical Chem.*, **30,** 1086, 1926), Marshall gives a mathematical analysis of the distribution of the light intensity at various points in the reaction vessel.

Determination of Reaction Velocity.—The methods used for the determination of the extent of chemical change are much the same as the ordinary methods of chemical kinetics. It is first of all necessary to find what the reaction products are and whether isolable intermediate products are formed. The reaction may be followed either by determination of the resultants formed or by determination of the decrease in concentration of reactants, and either chemical or physical methods may be employed. A convenient method for gas reactions in which the number of molecules changes is the determination of change of pressure at constant volume, or of change of volume at constant pressure. Other physical methods which may be employed are (1) the determination of electrical conductivity, used by Warburg (*Sitzungsber. Preuss. Akad. Berlin*, p. 960, 1919) in investigating the reversible transformation of maleic and fumaric acids; (2) measurement of changes of absorption due to the formation or disappearance of a coloured substance [Vranek (*Z. Elektrochem.*, **23,** 336, 1917), decomposition of potassium cobaltioxalate]; (3) thermal analysis [Eggert and co-workers, in investigating the bromine-sensitised reactions of the ethyl ester of maleic acid]; and (4) potentiometric methods [Rideal and Norrish (*Proc. Roy. Soc.*, **103** A, 357, 1923), decomposition of $KMnO_4$].

In cases where physical methods are not applicable, recourse is made to the methods of chemical analysis, and in kinetic studies samples of the reaction mixture are removed and analysed by volumetric or other methods. In such cases, it may be necessary to take into account a factor without influence on homogeneous thermal reactions, viz. the change in volume brought about by the withdrawal of the sample. The accurate estimation of the extent of photochemical change is often a matter of considerable difficulty owing to the small quantities of material transformed. This is particularly the case when monochromatic illumination is employed, when necessarily the intensity cannot be very high. Precautions must then frequently be taken to guard against loss of reaction product—by side reactions—before analysis. An excellent example of accurate technique in the estimation of small quantities of reaction product is afforded by Warburg's results for the photochemical decomposition of HI, where in each experiment less than 10^{-5} gram-equivalents of iodine had to be determined (*Sitzungsber. Preuss. Akad. Berlin*, p. 300, 1918).*

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* Forbes (*J. Physical Chem.*, **32,** 482, 1928) in an excellent summary of the experimental technique of photochemical reactions, gives the following

Many photochemical reactions may be investigated by a dynamic method in which the reactants are swept through the illuminated cell and then analysed. This method is particularly useful when reaction products which absorb the activating light are formed; by using large quantities of reactants which are illuminated only for a short time, detectable quantities of resultants are obtained. A modification of this method employed by Marshall (*J. Physical Chem.*, **30**, 1078, 1926) is to circulate the reactants repeatedly through the insolated reaction vessel, the products of the reaction being continuously removed by condensation, absorption, or other suitable method. Finally, some photochemical reactions are accompanied by the same process occurring as a thermal ("dark") reaction. If this is the case, the effect of the latter may be minimised by working at the lowest possible temperature; in any event, the rate of the "dark" reaction should be separately measured. The treatment of results when simultaneous "light" and "dark" reactions occur is given later (p. 667).

PHOTOSTATIONARY STATES.

Just as a thermal equilibrium is maintained by the equivalence of the reaction velocities of two opposing reactions, a photochemical equilibrium or photostationary state is obtained when the velocities of two opposing reactions, of which at least one is light-sensitive, become equal under the influence of a given illumination. The photostationary state is maintained at the expense of the light energy absorbed; so long as the intensity and quality of the light, together with temperature and pressure of the system, are kept constant, the composition of the system remains unaltered, but on removal of the light source the system changes or tends to change in the direction of the thermal equilibrium under the given temperature and pressure. When a photostationary state is attained, all the energy afterwards absorbed is converted into heat. In general, the term photostationary state may be limited to cases in which illumination produces a final composition of the system which is perceptibly different from that corresponding to thermodynamic equilibrium. The question as to whether a detectable shift in chemical equilibrium will or will not

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figures in illustration of the small amounts of chemical change which may normally be brought about using monochromatic light. For a process which obeys Einstein's Law, to form 10^{-3} moles. of product $3{\cdot}3 \times 10^{9}$ ergs must be absorbed using light of 366 $\mu\mu$. A mercury vapour lamp of standard type (consuming 2·2 amps. at 10 volts per cm.) will deliver 8×10^{3} ergs/sec. at wave-length 366 $\mu\mu$ and of a certain—reasonable—degree of monochromatism. It would therefore require—assuming all the light to be absorbed in the reacting system—110 hours to form 1 millimole of product. With light of 280 $\mu\mu$, 3000 hours' illumination would be required. Such figures make clear how it is that, unless a reaction has quantum yields much greater than those predicted by Einstein's Law, purity of light must be sacrificed in favour of intensity. Also, it is likely that future progress in photochemistry will entail developments in microchemical methods for the accurate estimation of very small quantities of reaction products.

be observed in a given case depends on several factors, the most important of which are the intensity and frequency of the light employed, the temperature of the system, the value of the thermal equilibrium constant, and (naturally) the sensitiveness of the methods of analysis employed. If the thermodynamic equilibrium constant is such that barely detectable quantities of (say) the reactants are present, and if light displaces the equilibrium still further towards the resultant side of the equation, then such a displacement effect becomes very difficult of detection. The effect of temperature may be regarded in the following manner. Two cases must be considered according as to whether the temperature is or is not high enough for thermal equilibrium to be established in a reasonable time. In the latter event if a photostationary state is reached, both direct and reverse reactions must be light-sensitive, and it is not possible to predict what effect change of temperature will produce on the photostationary state. In general, the temperature coefficients of both photo-reactions will be small and approximately equal, so that very little effect on the photo-equilibrium is to be anticipated on increasing the temperature. This would appear to be the case for most of the equilibria in gaseous systems investigated at ordinary temperatures (cf. the $SO_2 - O_2 - SO_3$ equilibrium, p. 381). On the other hand, if the temperature be high enough for thermal equilibrium to be established fairly rapidly, we may in general predict that the displacement from thermodynamic equilibrium caused by illumination will become smaller as the temperature is increased. Considering first the case when the reverse reaction is not light-sensitive, the photostationary state at a given temperature will then be defined by equality of the direct reaction (partly thermal, partly photochemical) and the thermal opposing reaction. The *displacement* from thermal equilibrium will depend on the velocities of the photochemical reaction and of the opposing thermal reaction, becoming greater with increasing velocity of the former and diminishing as the velocity of the latter increases. Since photochemical reactions possess considerably smaller temperature coefficients than do thermal reactions, it follows that increase of temperature causes a proportionally greater increase in the thermal reaction velocity, and consequently a smaller displacement from the thermal equilibrium. This conclusion has been experimentally verified by Luther and Weigert (*Z. physikal. Chem.*, **51,** 297, 1905 ; **53,** 385, 1905) in the case of the anthracene-dianthracene equilibrium.

An example of a photochemical equilibrium in which both direct and reverse reactions are photosensitive and which has been investigated at a temperature at which thermal equilibrium is easily established, is the formation and decomposition of phosgene, $CO + Cl_2 \rightleftharpoons COCl_2$. In this case, Weigert (*Ann. Physik* [iv.], **24,** 55, 1907) could detect no displacement from thermal equilibrium on illuminating the system at a temperature of 500°.

Coehn and Stuckardt (*Z. physikal. Chem.*, **91,** 722, 1916) distinguish three types of photostationary states for which respectively :

(1) Only one of the reactions concerned in the equilibrium is light-sensitive. The photostationary state is then attained when the velocity of the direct photochemical reaction (necessarily accompanied by a gain in free energy) becomes equal to that of the reverse " dark " reaction. An example is the photo-polymerisation of anthracene to the dimeride, a definite photostationary state being reached at suitable temperatures. When the velocity of the reverse " dark " reaction is inappreciable, the photo-process goes practically to completion. Such a case is the photochemical decomposition of ammonia by ultraviolet light, investigated by Regener (*Sitzungsber. Preuss. Akad. Berlin*, p. 1228, 1904) and by Coehn and Prigeant (*Z. Elektrochem.*, **20,** 136, 1914). Here, complete decomposition into N_2 and H_2 may be experimentally realised, owing to the extreme non-reactivity of the nitrogen molecule.

(2) Both direct and reverse reactions are sensitive to light, and to light of the same wave-length. An example is afforded by the equilibrium $2O_3 \rightleftharpoons 3O_2$ at high pressures. With increasing density, the long wave limit of the absorption band of oxygen is progressively displaced towards the visible, and if the pressure is sufficiently high (100 atm.), marked absorption of radiation of wave-length 254 $\mu\mu$ occurs. Warburg (*Sitzungsber. Preuss. Akad. Berlin*, p. 216, 1912; *ibid.*, p. 872, 1914) has shown that under such conditions both ozonisation and deozonisation take place.

(3) Both reactions are light-sensitive, but to different wave-lengths. Examples quoted by Coehn and Stuckardt are the formation and decomposition of O_3, HCl, $COCl_2$, H_2O, and CO_2. It is possible that under suitable experimental conditions, many of the cases in this category could be classed under (2); the $O_3 - O_2$ equilibrium has been cited as such a case, the equilibrium $CO + Cl_2 \rightleftharpoons COCl_2$ at high temperatures is another.

Photostationary states in gaseous systems have been systematically studied mainly by Coehn and his co-workers. The following are among the equilibria studied by them: $H_2 + Cl_2 \rightleftharpoons 2HCl$, $H_2 + Br_2 \rightleftharpoons 2HBr$, $H_2 + I_2 \rightleftharpoons 2HI$, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, $2CO + O_2 \rightleftharpoons 2CO_2$, $CO + Cl_2 \rightleftharpoons COCl_2$, and $2H_2 + O_2 \rightleftharpoons 2H_2O$. In discussing certain of the results obtained in these investigations, it is necessary to bear in mind that the photostationary state is always dependent on the nature of the light source employed, in particular, on the distribution of the intensities of the individual wave-lengths within the activating range, and that with different sources of light large shifts in the photo-equilibrium state might be found.

The Equilibrium: $2SO_2 + O_2 \rightleftharpoons 2SO_3$.—One of the most studied of these photochemical equilibria is the formation and decomposition of SO_3, investigated by Coehn and Becker (*Z. Elektrochem.*, **13,** 545, 1907; *Z. physikal. Chem.*, **70,** 88, 1909). The apparatus employed permitted of the investigation of photostationary states at temperatures up to 150°, and, as the quartz reaction vessel was built into a quartz mercury lamp, an illumination rich in ultra-violet rays and practically homogeneous in the insolated system could be obtained. Tubes containing SO_3 or mixtures of SO_2 and O_2 were insolated and the gas allowed to reach the photostationary state corresponding to the experimental conditions. The latter were such that neither thermal formation nor decomposition of SO_3 occurred at measurable speed. At a temperature of 45°, at which SO_3 is practically undecomposed when in thermal equilibrium, the photostationary state obtained corresponded to 35 per cent. decomposition. Experiments with mixtures of SO_2 and O_2 in various proportions and with SO_3 at different pressures led Coehn to believe that the photostationary state was governed by the law of mass action, but later work with other systems shows that any agreement obtained in this case with the mass action expression is entirely fortuitous. Since, in photochemical equilibria, at least one of the opposing reactions is sensitive to light, and velocities of photochemical reactions are not governed by the same laws as hold for " dark " reactions, there is no reason to expect that the law of mass action will apply to the photostationary state.

With increasing intensity of light (i.e. increasing current consumption of the lamp), the extent of decomposition of SO_3 at the photostationary state increases. This result is, however, probably due more to a change in the average wave-length than to a change in the intensity of the light, since with increasing current the intensities of the short wave ultra-violet lines increase relatively more than do those of the visible and longer wave ultra-violet lines. Using a different apparatus, Coehn established that this equilibrium is practically independent of temperature between 50° and 800° C. In the absence of a catalyst, neither thermal formation nor decomposition of SO_3 occurs at a measurable speed within this temperature range, so that this result implies equality of the temperature coefficients of the two opposing (photochemical) reactions.

The Photo-equilibrium: $2H_2O \rightleftharpoons 2H_2 + O_2$.—This equilibrium was investigated (Coehn, *Ber.*, **43,** 880, 1910) in the apparatus above described at a temperature of 150°. The photostationary state found corresponded to about 0·2 per cent. dissociation of water vapour, i.e. to the thermal equilibrium state at a temperature of 2000°. The conditions of illumination were the same as those which brought about 35 per cent. decomposition of SO_3. Further work by Coehn and Grote (*Nernst Festschrift*, 1912) showed that the law of mass-action is not here obeyed. The degree of dissociation (x) of water vapour at the photostationary state was found to be approximately inversely proportional to the pressure (P), i.e. $xP =$ constant, while if the law of mass action were followed the relation anticipated would be $x\sqrt[3]{P}$ $=$constant. Increase in light intensity causes an increased dissociation of water-vapour at equilibrium, i.e. the photostationary state is shifted in the direction in which work is performed on the system. The question of the reaction mechanism will not be considered at present, but it is to be observed that undoubtedly in this case a large number of reactions are possible and probably do intervene. Coehn and Grote found that if a mixture of H_2 and O_2 were passed rapidly through the insolated central quartz vessel, H_2O_2 could be detected in the issuing gas, but none was found present in static experiments or when the gases were passed *slowly* through the apparatus. H_2O_2 therefore appears as an intermediate product, as also in all probability does ozone; the presence of these substances makes very probable a large number of secondary reactions. In this connection, the work of Tian (*Ann. Physique*, (9), **5,** 248, 1916) on photostationary states in the system H_2, O_2, H_2O_2, H_2O is of interest If water be subjected to light containing short wave ultra-violet radiation ($\lambda =$ 190 $\mu\mu$) decomposition takes place, and according to Tian an equilibrium is set up of the type $2H_2O \rightleftharpoons H_2O_2 + H_2$. If the water contains dissolved oxygen, the latter reacts with hydrogen under the influence of light, and the diminished concentration of hydrogen thus produced involves an increased stationary concentration of H_2O_2. At the same time ozone formation and decomposition occur by different processes to some extent, as well as reactions diminishing the amount of H_2O_2. It will be seen that this is a very complex system, and that the photostationary concentration of H_2O_2 attained will depend on a variety of factors.

The Equilibria: $CO + Cl_2 \rightleftharpoons COCl_2$ and $2CO + O_2 \rightleftharpoons 2CO_2$.—As already mentioned, a photostationary state is also reached in the reaction $COCl_2 \rightleftharpoons CO + Cl_2$, though, using light transmitted by glass, Weigert (*loc. cit.*) could detect no displacement from thermal equilibrium at a temperature of 500°. With their quartz apparatus, however, Coehn and Becker (*Ber.*, **42,** 130, 1910) showed that $COCl_2$ at ordinary temperature was decomposed to the extent of 3·3 to 4·0 per cent. when photo-equilibrium was attained. The decomposition was found to be due to short wave ultra-violet light, since practically no carbon monoxide and chlorine were obtained when $COCl_2$ was insolated with light transmitted by uviol glass.

An apparatus of essentially similar construction, but of a simpler type and not permitting of regulation of the temperature in the reaction vessel independently of the lamp temperature, was employed by Coehn and Sieper (*Z. physikal. Chem.*, **91,** 347, 1916) to investigate the photochemical equilibrium $2CO + O_2 \rightleftharpoons 2CO_2$. The temperature employed was 240°. With light of constant intensity and containing wave-lengths less than 220 $\mu\mu$, the percentage decomposition of CO_2 at equilibrium increases with decreasing pressure more strongly than corresponds to the law of mass-action; it is approximately inversely proportional to the pressure. The interesting fact was observed that the photo-decomposition of CO_2 is remarkably sensitive to water vapour. At atmospheric pressure and under the experimental conditions of Coehn and Sieper, well-dried * CO_2 is decomposed at equilibrium to the extent of 18 per cent., but the addition of a small amount of water vapour reduces the decomposition to the barely detectable extent of 0·1 per cent. Coehn and Tramm (*Z. physikal. Chem.*, **105,** 356, 1923) showed that the reverse reaction, the combination of CO and O_2, takes place with the same velocity whether the gases are thoroughly dried or wet. The shift in the photo-equilibrium produced by water vapour is therefore not due to a positive catalytic effect of this latter on the rate of combination of CO and O_2 but to a retarding effect of H_2O on the decomposition of carbon dioxide. They also showed that traces of SO_2 had the same effect as water on this reaction.

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* But not intensively dried in the Bakerian sense. The influence of very small traces of water vapour on photochemical reactions is considered in Chapter XII.

Photochemical Formation and Decomposition of the Halogen Acids.—Coehn and Stuckardt (*Z. physikal. Chem.*, **91,** 722, 1916) investigated the action of light on gaseous HI, HBr, and HCl and on mixtures of hydrogen with the halogens. The resulting photostationary states were determined employing light transmitted by (*a*) quartz, (*b*) uviol glass, and (*c*) Jena glass. The apparatus used was similar to that of Coehn and Sieper (*loc. cit.*), and the temperature was in the neighbourhood of 270°. The following table summarises the results obtained:—

Equilibrium.	In Quartz. $\lambda > 220\ \mu\mu$.		In Uviol Glass. $\lambda > 254\ \mu\mu$.		In Jena Glass. $\lambda > 300\ \mu\mu$.	
	Decomposition.	Formation.	Decomposition.	Formation.	Decomposition.	Formation.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
$2HI \rightleftharpoons H_2 + I_2$	92·3	7·6	100	0	100	0
$2HBr \rightleftharpoons H_2 + Br_2$	100	0	20	80	0	100
$2HCl \rightleftharpoons H_2 + Cl_2$	0·42	99·58	0	100	0	100

In the case of the photo-decomposition of HI, the equilibrium position was attained very quickly (in 10 minutes) when a quartz vessel was used, and the same equilibrium point was reached starting with equivalent quantities of H_2 and I_2. In absence of short wave ultra-violet, no combination of H_2 and I_2 could be detected, the photo-equilibrium lying at 100 per cent. decomposition; while the rate of decomposition of HI was considerably smaller than that obtained using light transmitted by quartz. With uviol glass vessels the decomposition had proceeded to the extent of 88·4 per cent. in 32 hours, and with glass vessels the velocitity of decomposition was still smaller, 17 hours' illumination producing only 21·5 per cent. decomposition. The thermal equilibrium at 270° corresponds to a decomposition of HI of 6·2 per cent.; it should be noted, however, that Bodenstein's work on the thermal formation and decomposition of HI (*Z. physikal. Chem.*, **13,** 94, 1894) shows that the velocities of both "dark" reactions are negligible at this temperature, so that the photostationary state here found using quartz vessels is due entirely to two opposed photochemical processes.

Decomposition of HBr in quartz vessels was found to occur with considerably smaller velocity than that of HI, complete decomposition requiring 4 hours. In uviol glass both formation and decomposition of HBr take place; the velocity of either process is, however, so small that equilibrium could not be attained in a convenient time, but was estimated to be at about 20 per cent. decomposition. In glass vessels no decomposition occurs and the combination reaction proceeds slowly to completion. The velocity of photochemical combination of hydrogen and bromine possesses a rather greater temperature coefficient than most photochemical reactions. Kastle and Beatty (*Amer. Chem. J.*, **20,** 159, 1898) found only a small rate of union at 100°, but a much greater one at 196°, while at ordinary temperatures the velocity is exceedingly slow (Pusch, *Z. Elektrochem.*, **24,** 336, 1918). The temperature coefficient of this photochemical reaction has been determined by Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, **114,** 225, 1925) who find it to be 1·5 between 218° and 160°.

For the photochemical equilibrium between H_2, Cl_2, and HCl, Coehn and Wassiljewa (*Ber.*, **42,** 3183, 1909), employing the apparatus of Coehn and Becker, had previously established the fact that a slight decomposition of HCl occurs in ultra-violet light. They obtained an equilibrium decomposition of 0·25 per cent., which agrees reasonably well with the figure given in the table of 0·42 per cent. Exclusion of short wave ultra-violet light now has the effect of shifting the photo-equilibrium to 100 per cent combination.

The Equilibrium: $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$.—Andrich, Kangro, and Le Blanc (*Z. Elektrochem.*, **25,** 229, 1919) investigated the photochemical changes in the system SO_2Cl_2, SO_2, Cl_2 under the influence of radiation of definite wave-lengths. Experiments were carried out at temperatures below 125°, a range for which Trautz (*Z. Elektrochem.*, **14,** 534, 1908) had found that the velocities of the "dark" reactions were inappreciable in the absence of a catalyst. On illumination, although side reactions occur to a certain extent, the main reactions are represented by $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$. On insolation of SO_2Cl_2 with radiation absorbed only by this substance and not by SO_2 or Cl_2 ($\lambda = 230 - 240\ \mu\mu$), decomposition into SO_2 and Cl_2 occurs, and the reaction proceeds smoothly to completion at both the temperatures 55° and 100°. Illumination of a mixture of SO_2 and Cl_2 by light absorbed only by SO_2 does not lead to any perceptible formation of SO_2Cl_2, but employment of light absorbed only by the chlorine causes SO_2Cl_2 formation and a photostationary state is eventually reached. The velocity of combination and probably the position of photo-equilibrium depend markedly, however, on the water content of the system. Drying reduces the velocity of photochemical combination of SO_2 and Cl_2 very considerably, and indeed later work by Tramm (*Z. physikal. Chem.*, **105,** 356, 1922) shows that if the partial pressure of water vapour is reduced to 0·004 mm. Hg, no measurable combination occurs on illumination. In presence of small partial pressures of water vapour, however, Le Blanc and his co-workers found the photo-reaction to take place with a convenient speed, and obtained photostationary states which were established the sooner the higher the temperature. For temperatures between 105° and 125°, the photostationary state lies on the SO_2Cl_2 side of the thermal equilibrium, and the same is probably true for a temperature of 55°. The lower the temperature, the more both equilibria are displaced towards the SO_2Cl_2 side. The photostationary state is conditioned by two opposing photo-reactions, the direct combination process and the reverse decomposition of SO_2Cl_2, *effected through the agency of the chlorine*. The latter is a photosensitised reaction, the energy absorbed by the chlorine being transferred to sulphuryl chloride and utilised in decomposing it. The authors' interpretation of their results was that this sensitised reaction is only possible when the SO_2Cl_2 concentration attains a value greater than that corresponding to thermal equilibrium, so that necessarily the photostationary state lies on the SO_2Cl_2 side of the thermal equilibrium and a connection exists between the two equilibria. This view, however, is unjustifiable, since under the experimental conditions employed the thermal reaction velocity is negligible, and there appears no way, other than by the actual occurrence of the opposing thermal reactions, by which the photochemical equilibrium could be affected by the thermal equilibrium. The shift in the photostationary state with temperature is rather the result of different temperature coefficients of the direct and of the (photosensitised) reverse processes, and there is no *a priori* reason why the photostationary state in this case should not lie on either side of the thermal equilibrium.

In certain experiments, the curious phenomenon of a reversal in the direction of reaction was observed, i.e. starting with SO_2 and Cl_2 the pressure of the system decreased, passed through a minimum, and rose again before the photostationary state was finally attained. Such behaviour must be attributed to poisoning of one or both processes, most probably by products of side reactions which undoubtedly occur to some extent.

Photochemical Equilibrium in Nitrogen Peroxide.—A recently investigated photo-equilibrium in a gaseous system is that obtained on illumination of nitrogen peroxide (Norrish, *J.C.S.*, p. 761, 1927). The photoactive constituent of the ordinary "dark" equilibrium mixture of N_2O_4 and NO_2 is the NO_2 molecule, and exposure of nitrogen peroxide to visible and long wave ultra-violet light leads to the establishment of a photostationary state represented by

$$N_2O_4 \rightleftharpoons 2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2.$$

The increase of pressure which occurs in illumination is due partly to the chemical change and partly to a heating effect caused by the absorbed light and by the heat evolved in the recombination of NO and O_2. The photostationary state may be displaced towards the left-hand side by addition of NO or of O_2, and in presence of excess of either gas the photochemical reaction may be completely suppressed. The results of the investigation are in agreement with the view that photochemical decomposition of NO_2 occurs on collision of a light-activated NO_2 molecule with a non-activated one.

The Polymerisation of Anthracene.—Simpler cases of photochemical equilibria than most of those already discussed are found when only one of the oppositely directed processes is light-sensitive. The best studied example is the polymerisation of anthracene to dianthracene in homogeneous solution, which occurs according to the scheme

$$2C_{14}H_{10} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} C_{28}H_{20}.$$

The component processes and the resulting photostationary states were thoroughly investigated by Luther and Weigert (*Z. physikal. Chem.*, **51,** 297, 1905 ; **53,** 385, 1905). In the dark the equilibrium point of the system over the range of temperature employed is such that no detectable quantity of dianthracene is present. The depolymerisation reaction thus goes practically to completion under these conditions ; also it is found to be unimolecular, to be uninfluenced by light, and to possess a high temperature coefficient (2·8 for 10°). On illumination of a solution of anthracene in phenetole or in anisole with light from a carbon arc, polymerisation occurs, and a definite photostationary state is eventually reached when the velocity of thermal depolymerisation attains a value equal to that of photochemical polymerisation. Comparatively simple behaviour is here found. The photostationary concentration of dianthracene depends essentially on the light absorbed and on the temperature. At constant temperature, it is found to be proportional to the incident light intensity and to the area illuminated, and inversely proportional to the volume of the reaction mixture. The same is true for the intrinsic velocity of the photochemical reaction $2C_{14}H_{10} \rightarrow C_{28}H_{20}$; i.e., after correcting for the effect of the reverse " dark " reaction, the polymerisation process depends on the variables light intensity, area illuminated, and volume, in exactly the same manner as does the photostationary concentration of dianthracene. Luther and Weigert also showed that the effective light in these experiments was completely absorbed in the first few millimetres insolated. It will be shown later (see p. 399) that, if we assume photochemical reaction velocity to be proportional to the light absorbed and if the reacting substance absorbs strongly, then

$$\frac{dx}{dt} = \frac{kI_0q}{V},$$

where $\frac{dx}{dt}$ = rate of photochemical reaction, I_0 = incident light intensity, q = area illuminated, V = volume of reaction system, and k is a constant dependent only on temperature. This formula is derived on the assumption that concentration differences produced in the system on illumination are continuously removed by rapid stirring, a condition fulfilled in Luther and Weigert's experiments.* The results above given are thus in agreement with the view that at constant temperature the photochemical reaction velocity is here determined solely by the light energy absorbed. Experiments at different temperatures gave for the "light" reaction a very small temperature coefficient (1·1 for 10°). It was also found that different solvents (e.g. benzene, toluene, xylol, anisole, and phenetole) exert only slight specific effects on the rate of polymerisation and on the photochemical equilibrium. It will thus be seen that at constant temperature the rate of increase of concentration of dianthracene is given by

$$\frac{dx}{dt} = \frac{kI_0q}{V} - k'x,$$

in which k' is the unimolecular velocity constant of the "dark" reaction, and x is the concentration of dianthracene. At the photostationary state $\frac{dx}{dt} = 0$, so that

$$\frac{kI_0q}{V} = k'x, \quad \text{and} \quad x = \frac{k}{k'} \cdot \frac{I_0q}{V}.$$

The photostationary concentration (x) of dianthracene is thus proportional to the product of light intensity and cross-sectional area of the beam of light, and inversely proportional to the volume of reaction system. The effect of increase of temperature on x is obtained by consideration of the temperature coefficients of k and k'. The former is 1·1 for 10°, the latter 2·8, so that

$$\frac{x_{t+10}}{x_t} = \frac{1\cdot 1}{2\cdot 8} = 0\cdot 39.$$

The experimentally determined ratio was 0·34.

It was stated in the preceding paragraph that the photostationary concentration of dianthracene is determined solely by the energy absorbed. This statement is not quite correct, however, since Luther and Weigert found that the concentration of dianthracene at photo-equilibrium increases slowly with increasing concentration of anthracene, even though the latter is originally present in sufficient amount for the light absorption to be practically complete. Thus, increasing the concentration of anthracene from 20 millimoles per litre (at which the extent of light absorption is already nearly complete) to 160 millimoles per litre has the effect of doubling the photostationary concentration of dianthracene; further increase in anthracene content exerts no effect. Attempts have been made by Byk (*Z. physikal. Chem.*, **62,** 454, 1908; *Z. Elektrochem.*, **14,** 460, 1908) and by Weigert (*Z. physikal. Chem.*, **63,** 458, 1908) to account on thermodynamic grounds for this effect of increased concentration of anthracene. The treatment adopted, in both cases similar and based on the generalised methods of thermodynamics, is, however, not suited to lead to further insight into the process, and as no results of general validity were obtained, we need not enter into discussion of these attempts.

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* The experiments were carried out in boiling solutions in anisole or phenetole, in which, therefore, rapid equalisation of concentration differences took place.

Results very similar to those given for the anthracene-dianthracene equilibrium were obtained by Weigert and Kruger (*Z. physikal. Chem.*, **85,** 579, 1913) for the corresponding polymerisation of methylanthracene. The reaction scheme may be written

$$2C_{14}H_9(CH_3) \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} C_{30}H_{24}.$$

The product dimethylanthracene, $C_{30}H_{24}$, is not a pure compound but a mixture of isomers. Photostationary states were obtained at temperatures of 170°, 160°, and 150° in phenetole solution, and it was found that the equilibrium concentration of dimethylanthracene depends on the variables light intensity, area illuminated, volume, and concentration of photosensitive substance in much the same manner as does the photostationary concentration of dianthracene investigated by Luther and Weigert.

Miscellaneous Examples.—We have seen that when only one of the component processes of the equilibrium is photosensitive, the shift in the equilibrium produced by illumination is increased by lowering the temperature. This behaviour, found for the anthracene-dianthracene equilibrium, is also exemplified by the action of light on sulphur (Wigand, *Z. physikal. Chem.*, **77,** 423, 1911; *Ann. Physik*, **29,** 1, 1911). The equilibrium established both in solution in CS_2, CCl_4, or benzene and also in liquid sulphur may be represented by $S_\lambda \rightleftharpoons S_\mu$, the latter form being the colloidal, insoluble modification. Only the process from left to right is photosensitive, and on illumination the "dark" equilibrium is displaced in favour of S_μ. At the melting point of sulphur, the liquid in thermal equilibrium consists practically completely of the soluble S_λ form; increase of temperature causes the formation of increasing quantities of S_μ. On illumination with blue or violet light, the shift in the equilibrium towards S_μ is greater the lower the temperature, owing to the value of the temperature coefficient of the reverse thermal reaction $S_\mu \rightarrow S_\lambda$ being greater than that of the direct photochemical change.

An interesting example of a similar kind of displacement of photochemical stationary state is afforded by the reversible process

$$2Fe^{\cdot\cdot} + I_2 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} 2Fe^{\cdot\cdot\cdot} + 2I',$$

studied quantitatively by Rideal and Williams (*J.C.S.*, **127,** 258, 1925). Here, however, the effect of the light on thermal equilibrium was decreased, not by increase of temperature, but by addition of KCl, which increases the velocities of the "dark" reactions. In absence of the effective light ($\lambda = 579\ \mu\mu$) and at a temperature of 25°, thermal equilibrium is not established in less than three months, though after 24 hours the reaction has proceeded to over 90 per cent. of its limiting value. In the presence of 1·5N KCl, however, the thermodynamic activities of reacting substances are so increased that equilibrium is reached in three hours. On illumination, since only the reaction from left to right is photosensitive, photostationary states are finally attained in which $[I_2]$ has been decreased. It was shown that, starting at the same temperature with mixtures in thermal equilibrium, illumination caused a much smaller displacement (i.e. decrease in concentration of I_2) in the presence of KCl than in its absence. Thus, with 1·5N KCl present, the difference between the iodine concentrations at thermal equilibrium and at photochemical equilibrium was—in arbitrary units—0·56, while in absence of KCl but under otherwise identical conditions, the decrease in I_2 content amounted to 2·50.

Turning again to cases in which both direct and reverse reactions are photosensitive, examples of photostationary equilibrium between *cis-* and *trans*-isomerides are known,* the best investigated case being the equilibrium between maleic and fumaric acids. Kailan (*Z. physikal. Chem.*, **87**, 333, 1914) has determined the photostationary states produced when aqueous solutions of maleic or fumaric acid are subjected to the action of ultra-violet radiation. The rate of reaction may be conveniently followed and the equilibrium position determined by measurement of the electrical conductivity. Neither reaction occurs in the dark at ordinary temperatures. Kailan found that the equilibrium state on illumination was essentially the same whether the containing vessel was made of glass or of quartz, so that change of the wave-length of the activating light exerts little effect on the photostationary state. The latter does depend, however, on the total concentration (maleic acid + fumaric acid), being displaced in favour of maleic acid with increasing total concentration (n). Thus with $n = 0·05$, at photo-equilibrium the percentage of total acid present as maleic acid was found to be 75 per cent.; with $n = 0·2$, the corresponding figure was 79 per cent. These figures are in agreement with those calculated by Warburg (*Sitzungsber. Preuss. Akad. Berlin*, p. 960, 1919) from his measurements of the quantum efficiencies of the two opposing photochemical reactions, maleic → fumaric and fumaric → maleic (see p. 476). The table on the following page gives the values calculated by Warburg. A displacement of the photostationary equilibrium with increasing total concentration as obtained by Kailan is here predicted; there would also appear to be an effect due to wave-length, since the figures for $\lambda = 253\ \mu\mu$ are lower in both cases than those for $\lambda = 207$ and $282\ \mu\mu$.

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* References to such cases will be found in Weigert's "Die Chemischen Wirkungen des Lichts," *Ahrens Sammlung*, **17**, 213, 1912, and in the Chemical Society's *Annual Reports for* 1925, p. 352 (Allmand).

$\lambda(\mu\mu)$.	Per Cent. Maleic Acid at Photo-equilibrium.	
	$n = 0{\cdot}0102$	$n = 0{\cdot}00306$
207	76·4	68·3
253	69·6	63·5
282	80·6	76·0
Mean	75·5	69·2

Interesting but conflicting results have been obtained from investigations on the photo-bromination of α-phenylcinnamonitrile. According to Plotnikow (*Z. wiss. Phot.*, **19,** 1, 1919) a photostationary state is eventually reached by the concurrence of the direct photo-reaction and the reverse "dark" reaction; Berthoud and Nicolet (*Trans. Faraday Soc.*, **21,** 557, 1926) find that the latter process is photosensitised by bromine and does not occur in the dark. They find that a photostationary state can be obtained which is independent of the intensity of the light and which satisfies the relation

$$\frac{\{k_1[\mathrm{A}] + k_2[\mathrm{ABr_2}]\}\,[\mathrm{Br_2}]}{[\mathrm{ABr_2}]} = K,$$

in which the nitrile is designated as A, and the brominated product is ABr_2. In cases in which $[ABr_2]$ is small compared with [A], the relation is simplified to

$$\frac{[\mathrm{A}][\mathrm{Br_2}]}{[\mathrm{ABr_2}]} = K_1,$$

i.e. the mass-action expression.

Plotnikow, on the other hand, finds that the equilibrium is displaced towards the dibromide side by increase in intensity of illumination. The increased intensity was obtained by placing a mirror at the back of the reaction vessel. The velocity of bromination when the absorption is weak is stated to be given by

$$\frac{dx}{dt} = kI_0^2(b - x)^2(a - x) - k_1x,$$

where a and b are initial concentrations of nitrile and bromine respectively and k_1 is the velocity constant for the "dark" decomposition of the dibromide. Berthoud's results appear to be the more acceptable (cf. p. 606, where the reaction mechanism is discussed).

Application of Theory of Photostationary States to Vision.—The photosensitivities of certain organisms and of the human eye have recently been interpreted in terms of mechanisms which explain the sensitivity on photochemical grounds and involve photostationary states. These ideas have been developed by several investigators, in particular by Hecht (*J. Gen. Physiology*, 1920-1926; *Naturwiss.*, **13,** 66, 1925). In the human eye, the rods and the cones of the retina from two different photosensitive systems, the rods alone functioning for very small light intensities (twilight vision), and the cones for high intensities. Simplification of the experimental conditions is obtained by the study of the photic activity of certain organisms, the best example being the mussel *mya arenaria*, which possesses neither iris nor lens, and apparently contains only one kind of photosensitive cell. The mechanism of light-sensitivity postulated is, however, essentially the same in both cases. The *mya*, when subjected to illumination, responds by the retraction of its siphon, and, just as does the human eye, it shows light and dark adaptation. The sensitivity of the organ to a given amount of light energy decreases on strong illumination, but slowly increases again when the animal is placed in the dark. The gain in photosensitivity in the dark is termed dark adaptation. It is assumed that in order to produce a minimal amount of excitation, a definite amount of photochemical substance in the sense organ must be destroyed, and that the photochemical reaction velocity is proportional to the concentration of the photosensitive substance S. At the beginning of dark adaptation, i.e. immediately on cutting off the light, the concentration of S is small, and increases continually to a maximum when adaptation is complete. According to Hecht, the velocity of dark adaptation (increase in S) follows the kinetics of a bimolecular reaction. Assuming then that two substances P and A unite to form S in the dark, the reaction underlying dark adaptation is written $P + A \rightarrow S$. As the light and dark reactions appear to be completely reversible, the total process on illumination may be written

$$S \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} P + A.$$

This equation has been successfully applied to the phenomena associated with photosensitivity in both the *mya* and the human eye. In either case, on illumination light adaptation is quickly established, which according to the theory corresponds to a photostationary state in which constant concentrations of S, P, and A are maintained. Such photo-equilibria will be defined as follows. Assuming that photochemical reaction velocity is proportional to incident light intensity (see p. 404), then the velocity of the photochemical process $S \rightarrow P + A$ at any instant is given by

$$\frac{dx}{dt} = k_1 I(a - x),$$

where $a - x$ is the concentration of S. The velocity of the reverse thermal reaction is

$$-\frac{dx}{dt} = k_2 x^2.$$

At the photostationary state, $\frac{dx}{dt} = 0$ and thus

$$KI = \frac{x^2}{a - x}, \quad \text{where } K = \frac{k_1}{k_2}.$$

This equation, which gives the relation between light intensity and photostationary concentrations (i.e. on light adaptation) has been tested and found to have correct consequences. The process of dark adaptation in the *mya* has the usual temperature coefficient of thermal reactions, indeed the rather high value 3·85 is found. The temperature coefficient of the photochemical process is also normal, the value found being 1·06.

The same theory also fits in with certain experimental data on human vision. Included here is the work on the Weber-Fechner Law. As already stated, the eye adapts itself rapidly to almost any intensity of illumination. If I = intensity to which the eye is adapted, and ΔI is the increase in that intensity which is just perceptible, the Weber-Fechner Law postulates direct proportionality between the two, i.e. $\frac{\Delta I}{I}$ = constant. The experiments of Koenig and Brodhun (*Sitzungsber. Preuss. Akad. Berlin*, p. 641, 1889) show, however, that this is only true over a limited range of intensities, and that the ratio $\Delta I/I$ increases for both higher and lower intensities (the same has also been found for the photosensitivity of *mya*). These deviations from the Weber-Fechner Law find their explanation in terms of the equation for the photostationary state. For adaptation to intensity I_1 we have

$$KI_1 = \frac{x^2}{a - x}.$$

At the slightly greater intensity $I_1 + \Delta I_1$ we have

$$K(I_1 + \Delta I_1) = \frac{x'^2}{a - x'}.$$

$x' - x$ thus gives the amount of S decomposed by ΔI_1. As in the analogous case for *mya*, we make the assumption that in order for the retinal elements to distinguish between one intensity and the next perceptible one, the change from the one to the other must involve a constant quantity of photosensitive material, i.e. $x' - x$ = constant. Comparing two intensities I_1 and I_2 ($I_2 > I_1$) and their corresponding increments ΔI_1 and ΔI_2, we obtain

$$I_1 = \frac{x_1^2}{(a - x_1)K}; \quad I_1 + \Delta I_1 = \frac{x_1'^2}{(a - x_1')K};$$

$$I_2 = \frac{x_2^2}{(a - x_2)K}; \quad I_2 + \Delta I_2 = \frac{x_2'^2}{(a - x_2')K};$$

from which

$$\frac{\Delta I_1}{I_1} = \frac{x_1'^2(a - x_1) - x_1^2(a - x_1')}{x_1^2(a - x_1')}$$

and

$$\frac{\Delta I_2}{I_2} = \frac{x_2'^2(a - x_2) - x_2^2(a - x_2')}{x_2^2(a - x_2')}.$$

When I_1 and I_2 are both small (i.e. x_1 and x_2 small) it may be shown that

$$\frac{\Delta I_2}{I_2}\bigg/\frac{\Delta I_1}{I_1} < 1,$$

so that at low intensities the ratio $\Delta I/I$ decreases with increasing intensity. On the other hand, when I_1 and I_2 are big (x_1 and x_2 nearly equal to a) the reverse follows, and $\Delta I/I$ increases with increasing intensity. Calculation of the data of Koenig and Brodhun on the basis of this equation shows that the form of the $\frac{\Delta I}{I} - I$ curve is well reproduced. Allowance is necessary for the fact previously mentioned that there is an intensity threshold for the cones, below and above which there are therefore different values for the unitary increments of quantity of photochemical action (i.e. different values for $x' - x$).

The photosensitive substance in the eye is undoubtedly visual purple (rhodopsin), first obtained by Boll. Visual purple is bleached on exposure to light; in the dark it is regenerated, completely in the retina, but only to a small extent in solution. Hecht has shown that the bleaching of solutions of visual purple is a simple photochemical reaction without period of induction or after-effects, that the velocity is proportional to the concentration (a relation which holds for nearly all photochemical reactions when the extent of absorption is small (cf. p. 399)), that the temperature coefficient is 1·0, and that the velocity is proportional to the light intensity. All these properties are in agreement with those postulated for the reaction $\mathrm{S} \rightarrow \mathrm{P} + \mathrm{A}$ in the retina. The absorption of visual purple in aqueous solution is a maximum at 503 $\mu\mu$. Experiments carried out by Hecht on the "visibility" of monochromatic light of weak intensities (the rods containing visual purple being the photosensitive system) made possible a determination of the relative energies in different parts of the spectrum necessary to produce "colourless" sensitivity. It is possible from the results to determine the absorption spectrum of the photosensitive substance in the retinal rods, and in this way a maximum absorption at 511 $\mu\mu$ was obtained. The slight displacement of 8 $\mu\mu$ from the absorption maximum of visual purple in aqueous solution was attributed by Hecht to the factors operating to produce Kundt's rule. Further evidence of the applicability of the conception of photostationary states to the problem of vision has been advanced; we have said enough, however, to indicate that a promising line of attack has been opened by this work, and must refer the reader for further details to the original papers.

PHOTOCHEMICAL KINETICS.

In discussing photochemical reaction velocity, it is necessary to consider the effects of two sets of factors—(*a*) those concerned with the radiation, and (*b*) the remaining factors, such as temperature, pressure, concentration of reacting substances and of catalysts, solvent, and the other variables which are found to exert an influence on the velocity of thermal reactions. The light factors comprise the nature of the light incident on the reaction system and the disposition of the latter with respect to the illumination. Of chief importance are the following: the wave-length and distribution of intensity of the radiation penetrating into the reaction mixture, the area illuminated, the nature of the optical path of the light in the system (e.g. whether reflection at a wall occurs or not), and finally the total volume of the reaction system.* The state of polarisation of the radiation does not affect the course of photochemical reactions in gases or liquids, though with solids different effects of polarised light and ordinary light have been observed in certain cases.† We shall not deal at present with the effect of variation of wave-length, but consider only the case in which practically monochromatic light is used. With simple disposition of apparatus, i.e. employing a reaction vessel with plane parallel ends and a uniform, parallel beam of light incident at right angles, it is possible to simplify the conditions so that the only light variable remaining is the intensity incident to the reaction system. Of the other factors, we shall limit the present discussion to the effect of concentrations of reacting substances; consideration of this together with the effect of light intensity is the chief problem of photochemical kinetics.

It is important to observe that in every photo-reaction a spatial variation in the intensity of illumination is automatically present; photochemically reacting systems are non-homogeneous with respect to light intensity. Owing to absorption, the intensity at a given instant decreases with increasing penetration of the light beam into the reaction mixture in accordance with Lambert's Law, $I = I_0 e^{-kd}$ (I_0 = the incident intensity, and I that at distance d). Since the reaction rate is intimately associated with the prevailing light intensity, the velocity of reaction will vary with distance traversed by the beam in the system, and thus local differences in the concentrations of reactants and resultants will be set up. Confining our attention to homogeneous systems (liquid or gaseous), these differences in concentration will tend to be neutralised by slow diffusion processes, and a complicated state of affairs ensues not very amenable to mathematical treatment. If, however, the reaction rate is not too high—

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* Strictly, of course, this is not a variable connected with the light, but, as shown later, it does enter into the equation for the reaction velocity in homogeneous systems.

† Weigert, *Verh. deut. phys. Ges.*, **21**, 479, 615, 623, 1919; *Z. Elektrochem.*, **26**, 357, 1920.

and this is in general true for photochemical processes under usual experimental conditions—concentration differences resulting from unequal reaction velocities at different points in the system may be neutralised by vigorous stirring. In such a case, it is permissible to consider that the system is homogeneous with respect to concentration throughout the course of an experiment. Dealing with the case in which the only *absorbing* constitutent of the system is a reactant, it is finally necessary to consider the variation of intensity with time, i.e. with diminishing concentration of reactant. If Beer's Law holds for the absorbing substance under the conditions of experiment, the light intensity at a point distant d from the point of entry of the light is given by $I = I_0e^{-acd}$, in which $c =$ concentration of reacting (and absorbing) substance at the given time t. An important part of the kinetics of a reaction receives solution when we are able to express the reaction velocity in terms of I_0 (the incident light intensity) and the concentrations of the reacting substances.

The introduction of the quantum theory gives a basis for the treatment of the problem, but no generalisations and no classification of reactions can be made as in the corresponding case of thermal reactions. In photochemical processes, light absorption takes place in quanta, and a certain fraction of the molecules is at any instant activated or endowed with a considerable excess of energy above that of the normal state. Thus a molecule which absorbs a quantum of light of wavelength 400 $\mu\mu$ gains in internal energy an amount equal to the kinetic energy of molecular translation at a temperature of 25,000°, so that its properties are quite different from those of the main bulk of non-activated molecules. Einstein's Law defines unequivocally the primary process in photochemical reactions; each quantum absorbed produces one activated molecule with an energy increment of $h\nu$ ergs. The primary process is, however, to be sharply differentiated from the total process. The latter includes the resultant effect of all the changes which are subsequent to the primary absorption. The energy absorbed and contained in the activated molecules may be utilised in different ways. While experimental evidence shows that we may in general disregard (a) ionisation or complete loss of an electron and (b) loss of energy by fluorescence, there still remain as possibilities (c) loss of energy by dissipation into thermal energy on collision and (d) transfer of energy of activation as such to other molecules by collision. If chemical reaction occurs, this may take place either spontaneously or on collision of the activated molecule with a reactant molecule or an indifferent one. We have above limited the primary process to quantum absorption of the light, but it is probable that, in certain cases, this is coincident with a dissociation of the molecule, e.g. $AB + h\nu \rightarrow A + B$. Whatever be the nature of the primary process, however, whether it is simply the formation of an activated molecule which may then react, or whether the primary absorption is simultaneously accompanied by a disruption of the absorbing molecule into atoms, the *net* photochemical reaction is never solely the primary process, but the intervention of further secondary chemical processes is inevitable. The latter processes may be of a very complicated nature, and this, taken in conjunction with the above-mentioned possibility of a complex scheme of energy transfers, makes the elucidation of the kinetics of many photochemical reactions a problem of considerable difficulty. In view of the distinction between primary and total reactions, the question of reaction mechanism becomes of fundamental importance to the study of the kinetics, and the two cannot be entirely separated. The velocity of the simplest photochemical reaction will depend on the relative speeds of at least three component reactions, which may be written

$$
\begin{aligned}
&(1)\ \mathrm{AB} + h\nu \rightarrow \mathrm{AB}^* \\
&(2)\ \mathrm{AB}^* \qquad\ \rightarrow \mathrm{AB} \\
&(3)\ \mathrm{AB}^*(+\mathrm{C}) \rightarrow \text{Resultants.}
\end{aligned}
$$

Here AB is the absorbing molecular species, C a non-absorbing reactant. In more complicated cases, further secondary reactions take place. Our knowledge of molecular excitation and of the properties of activated molecules (or of atoms) is at present insufficient to enable us to do more than make plausible hypotheses as to the nature of the primary and secondary processes, i.e. the reaction mechanism. We shall not, however, pursue the question of mechanism further at present, but deal with kinetics from a more formal standpoint.

Application of the Stark-Einstein Law gives directly the velocity of the primary process in terms of the energy absorbed, and thus, if certain conditions apply, in terms also of the incident light intensity. If now in a given experiment all or a constant fraction of the molecules which absorb succeed in reacting to produce the finally observed reaction products, the velocity of the net process will depend only on the light energy absorbed. The condition postulated is more accurately stated in terms of two presumptions—(*a*) that, independent of the concentration terms, a constant fraction of absorbing molecules enters into reaction, and (*b*) that the number of molecules of final product formed from each light-activated molecule which reacts is constant throughout the course of the change. The factors which obviously exercise a decisive influence in this connection are the average life of the activated molecules, the frequency and the nature of the collisions suffered by the activated molecule, and the nature of the secondary processes. Postponing consideration of these matters until the succeeding Chapter, it will be seen that if the above conditions hold, comparatively simple kinetic behaviour is to be anticipated, viz. direct proportionality between absorbed energy and reaction velocity. This relation is found to be true, or at least approximately so, in a surprisingly large number of photochemical reactions, and this form of dependence of reaction velocity on absorbed energy, independent of other factors, may be regarded as the typical photochemical case. We will therefore derive the kinetic equations for such behaviour †

† The derivation given is that of Wegscheider (*Z. physikal. Chem.*, **103**, 273, 1923).

and reserve treatment of other cases until reaction mechanism is considered.

For a reaction whose velocity is at all stages proportional to the rate of absorption of energy, consider the action of monochromatic light of constant intensity, and let dL be the radiant energy absorbed in volume dv in unit time. Then

$$\frac{dx}{dt} \,.\, dv = k \,.\, dL \quad . \quad . \quad . \quad . \quad (1)$$

in which dx = number of moles of photolyte transformed in time dt and in unit volume. k is the proportionality constant between absorbed light energy and amount of material transformed, and, if Einstein's Law holds for the particular process studied, is equal to

$$\frac{1}{N_0 h\nu} \text{ } (N_0 = \text{Avogadro Constant}).$$

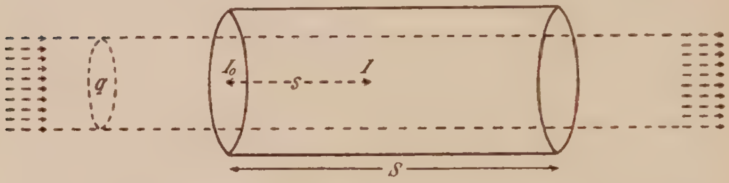

FIG. 44.

We shall deal with the case of an irreversible homogeneous photochemical reaction which proceeds only on illumination and in which the absorbing substance disappears. Concentration differences in the solution are neutralised by rapid stirring. The illumination is effected by a homogeneous parallel beam of monochromatic light entering the system at right angles to a plane surface and emerging from the system at a parallel wall (or completely absorbed therein).* The reaction vessel need not, however, be completely illuminated, but, as shown in Fig. 44, the cross-section of the beam may be less than the cross-sectional area of the reaction vessel. Finally, only one absorbing molecular species is present throughout the change.

Let q = cross-sectional area of beam,
S = length of beam in reacting system,
s = distance of an arbitrary point (in the path of beam) from place of entry of light,
I_0 = incident light intensity,
I = intensity at the arbitrary point,
a = initial concentration of absorbing (and reacting) species,
$a - x = c$ = concentration at time t,
V = volume of reaction mixture.

---

* I.e. no reflexion back into the reaction mixture is supposed to occur.

In the infinitely narrow volume element qds, in which the concentration of the absorbing substance is c, the concentration change (dz) in the time dt is, from equation (1), represented by

$$dz \,.\, qds = k \,.\, dL \,.\, dt,$$

and since, if Beer's Law holds,

$$dL = I\alpha c \,.\, qds \qquad (\alpha = \text{molecular absorption coefficient}),$$

we have $$dz \,.\, qds = kI\alpha c \,.\, qds \,.\, dt,$$
and therefore $$dz = kI\alpha c \,.\, dt.$$

At time t, $c = a - x$ and $I = I_0 e^{-\alpha cs}$,

hence $$dz = k\alpha I_0 e^{-\alpha(a-x)s} \,.\, (a - x)dt \quad . \quad . \quad . \quad (2)$$

The transformation occurs only in the illuminated volume qS. The total transformation in time dt is thus

$$\int_{s=0}^{s=S} qds \,.\, dz.$$

Since stirring causes the transformation to be divided equally over the whole volume V, in which the concentration change dx results, it follows that

$$\int_{s=0}^{s=S} qds \,.\, dz = V \,.\, dx,$$

or

$$V \,.\, dx = k\alpha I_0(a-x)q \,.\, dt\int_{s=0}^{s=S} e^{-\alpha s(a-x)} \,.\, ds = kI_0 q[1-e^{-\alpha S(a-x)}] \,.\, dt \quad (3)$$

Introducing the initial conditions $t = 0$, $x = 0$, integration yields

$$\frac{k\alpha I_0 qSt}{V} = \alpha Sx + \log_e \frac{1 - e^{-\alpha Sa}}{1 - e^{-\alpha S(a-x)}} \quad . \quad . \quad . \quad (4)$$

If the reaction vessel is a parallelopiped and completely illuminated, then $V = qS$, and V does not appear in the equation.

Equation (4) is the general solution of our problem. Two limiting cases of the equation are of importance:—

(1) *Strong Absorption of the Light*, i.e. αSa large. When the light is strongly absorbed, it is seen that the second term on the right-hand side of equation (4) may be neglected (since it approaches the value log 1), and we obtain

$$x = \frac{kI_0 qt}{V} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The amount of material transformed is thus proportional to the time, i.e. the reaction velocity is constant throughout the experiment; hence the reaction is of *zero order*.

(2) *Weak Absorption of the Light*. With very weak absorption (αSa small), the term αSx of equation (4) may be neglected, and the

exponentials in the numerator and denominator of the logarithmic term may be expanded into series ($e^{-x} = 1 - x + \frac{x^2}{2} - \ldots$) and only the first two terms of the expansion taken. We then obtain

$$\frac{k\alpha I_0 qS}{V} = \frac{1}{t}\log_e\frac{a}{a-x} \qquad . \quad . \quad . \quad (6)$$

the equation of a *unimolecular* reaction.

The general solution (equation (4)) represents an apparent order of reaction between 0 and 1; it is clear that the "order" will be nearer 0 the greater the absorption, and that it increases as the reaction proceeds, tending towards unity as x approaches a. When the absorption is complete, equation (5) is followed, the reaction velocity being independent of the concentration, and when the absorption is feeble, we have a reaction of the first order (equation (6)), i.e. velocity proportional to concentration of photolyte.

Many examples of the applicability of equation (5)—independence of reaction velocity on concentration when the absorption is high—are found. We may cite the decomposition of ammonia in ultraviolet light (Regener, *Sitzungsber. Preuss. Akad. Berlin*, p. 1228, 1904; Warburg, *ibid.*, p. 746, 1911; Kuhn, *Compt. rend.*, **177,** 956, 1923), the transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid with light of wave-length 366 $\mu\mu$ (Weigert and Kummerer, *Ber.*, **46,** 1207, 1913; Weigert and Brodman, *Trans. Faraday Soc.*, **21,** 453, 1926), and the hydrolysis of monochloracetic acid (Rudberg, *Z. Physik*, **24,** 247, 1924). Reactions in which the order lies between zero and unity are the bromination of toluene (Bruner and Czarnecki, *Bull. Acad. Sci. Cracow*, p. 516, 1910), the polymerisation of anthracene (Luther and Weigert, *Z. physikal. Chem.*, **51,** 297, 1905), the decomposition of sodium hypochlorite solutions (Spencer, *J.C.S.*, **105,** 2565, 1914), and the decompositions of chlorine monoxide and dioxide in CCl_4 solution (Bowen, *J.C.S.*, **123,** 1199, 1923). It is of interest that the first photochemical process to be investigated kinetically—the decomposition of HI (Bodenstein, *Z. physikal. Chem.*, **22,** 23, 1897)—was found to be unimolecular (weak absorption of the effective light), whereas the corresponding thermal reaction is bimolecular.

Though the order of a large percentage of photochemical reactions is found to lie between 0 and 1, it does not follow that equation (4) necessarily represents the course of the reaction. In order for this to be true, the conditions postulated in its deduction must apply; in particular, the reaction velocity must be strictly proportional to the rate of absorption of energy and Beer's Law must be applicable to the absorbing substance throughout the course of the reaction. It is probable that in the majority of cases one or both of these conditions ceases to apply, and that, though the apparent order increases as the reaction progresses, equation (4) is not obeyed. The kinetics of very few photochemical reactions under the influence of monochromatic light have, however, been sufficiently investigated to permit of stating to what degree of exactness the predicted course is followed.

Though the apparent order of most photochemical reactions lies between 0 and 1, there are a few cases in which is found a higher order with respect to the absorbing constituent. The first of such cases to be discovered was the decomposition by ultra-violet light of ozone in mixtures with oxygen (Weigert, *Z. physikal. Chem.*, **80,** 78, 1912; *Z. Elektrochem.*, **18,** 654, 1912). The reaction order lies between 1 and 2, and decreases with increasing extent of absorption. A reaction order of 2 is also observed for the same reaction in visible light (Griffith and Shutt, *J.C.S.*, **123,** 2752, 1926); the absorption of ozone in this region of the spectrum is weak. Other cases of a bimolecular course are the hydrolysis of the chloroplatinic acids (Boll and Job, *Compt. rend.*, **154,** 881; **155,** 826, 1912; Boll, *Ann. Physique*, (9), **2,** 5, 226, 1914), the combination of hydrogen and chlorine (Bodenstein and Dux, *Z. physikal. Chem.*, **85,** 297, 1913), the decomposition of potassium cobaltioxalate (Vranek, *Z. Elektrochem.*, **23,** 336, 1917), and the bromination of α-phenylcinnamonitrile (Plotnikow, *Z. wiss. Phot.*, **19,** 1, 1919). In each of the last three examples, however, some doubt exists as to the true order. The hydrogen-chlorine reaction will be discussed later (see Chapter X.). The bromination of α-phenylcinnamonitrile has been re-investigated by Berthoud and Nicolet (*Trans. Faraday Soc.*, **21,** 557, 1926), who find that the reverse reaction, regarded by Plotnikow as a "dark" reaction, is really photosensitised by bromine. According to the Swiss investigators, the true order for weak absorption is 1·5. The decomposition of potassium cobaltioxalate was found to be bimolecular in non-homogeneous light when the absorption is weak, but apparently, since the quantum efficiency of the process is independent of the concentration, the reaction is unimolecular in monochromatic light.

In non-sensitised reactions involving a non-absorbing reactant, the order with respect to the latter is very often zero. This has been observed for the photo-reaction between chlorine and $CBrCl_3$; here dilution with $SiCl_4$ or CCl_4 has no influence on the velocity, which is determined solely by the energy absorbed by the chlorine and is independent of the concentration of the non-absorbing reactant $CBrCl_3$. It is clear, however, that such independence can only hold for concentrations above a certain limiting value; a decrease in concentration of $CBrCl_3$ below this limit will cause a decrease in velocity of reaction, and this implies an increase in the order with respect to the non-absorbing component. A similar independence of reaction velocity on the concentration of non-absorbing reactant is found in the reaction between bromine and hexahydrobenzene (Meidinger, quoted by Noddack, *Handbuch der Physik*, Vol. XXIII.), and the same is approximately true for the photochemical oxidation of quinine by chromic acid (Luther and Forbes, *J. Amer. Chem. Soc.*, **31,** 770, 1909). In the latter reaction the quinine is the light-sensitive component, the absorption of the chromic acid only affecting the course of the reaction by "internal light-filter" action. It would appear that in nearly all cases the order for a non-absorbing reactant never exceeds unity, and that generally in concentrated solutions the velocity tends to become independent of the concentration of this component, i.e. the order tends to a limiting value of zero.

In sensitised reactions the concentration of the absorbing substance remains unchanged, so that strictly it is not permissible to speak of an order with respect to the sensitiser. If, however, we compare velocities in systems with different concentrations of sensitiser, it is found as a general rule that in such reactions the velocity is determined by the rate of energy absorption, and as this depends on the extinction, the reaction order with respect to the sensitiser may be stated as lying between 0 and 1. As regards the order with respect to the reactants in sensitised reactions, a remarkable persistence of zero order down to very low concentrations has been observed in certain cases. Thus, in the decomposition of ozone sensitised by chlorine, there action velocity under constant illumination remains constant throughout the whole course of the decomposition, or at least to partial pressures of ozone less than 0·5 mm. Hg.

A similar strong persistence of zero order down to very low concentrations of reactant is also observed in the following bromine-sensitised reactions: the decomposition of ozone, the oxidation of $CBrCl_3$ in CCl_4 solution by dissolved oxygen, and the conversion of the ethyl ester of maleic acid into fumaric ester in CCl_4 solution. In other sensitised reactions the reaction velocity is found to depend on the concentration of reactants, though frequently in a somewhat unexpected manner. Thus, in the chlorine-sensitised formation of water from hydrogen and oxygen—a reaction discovered by Weigert (*Ann. Physik*, **24,** 243, 1907) and re-investigated by Norrish and Rideal (*J.C.S.*, **127,** 787, 1925)—the reaction velocity is found to be proportional to the product of the energy absorbed (by the chlorine) and the concentration of oxygen, and to be independent of the hydrogen concentration within wide limits.* On the other hand, in the same reaction sensitised by mercury vapour (Marshall, *J. Physical Chem.*, **30,** 34, 1926), the kinetic equation (for constant energy absorption) is found to be of the form $\frac{dx}{dt} = \frac{k[H_2]}{[H_2] + [O_2]}$. The mechanisms proposed to account for these results will be considered later, as also will other examples of photosensitisation; it will be appreciated, however, that the different kinetic courses of this reaction in the presence of the two sensitisers imply two entirely different reaction mechanisms.

Reverting again to reaction order with respect to an absorbing

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* According to Cremer (*Z. physikal. Chem.*, **128,** 285, 1927), however, the velocity of water formation in this process is given by

$$\frac{dx}{dt} = kI_0[Cl_2],$$

and is independent of the oxygen concentration.

reactant, we have seen that in most photochemical reactions the "true order" * is one or, in a few cases, two. Recent work has shown, however, that these alternatives do not exhaust the possibilities, as well-investigated cases have been found in which the order is 0·5 (and 1·5). The photochemical union of hydrogen and bromine according to Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, **114**, 208, 1924) follows a reaction course very similar to that obtaining in the dark. For the case of weak absorption, the kinetic equation is

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}]\sqrt{I_0[\mathrm{Br_2}]}}{1 + \dfrac{[\mathrm{HBr}]}{10[\mathrm{Br_2}]}}.$$

The velocity of combination is thus proportional to the concentration of the non-absorbing reactant hydrogen, and, in the initial stages of the reaction when the second term of the denominator may be neglected, proportional also to the square root of the bromine concentration. When the absorption is complete, the order with respect to bromine at the start, when no HBr is present, becomes zero. Another well-investigated case in which fractional powers of the concentration of absorbing reactant appear is the photochemical reaction between potassium oxalate and iodine (Berthoud and Bellenot, *J. Chim. phys.*, **21**, 308, 1924). For feeble absorption, the reaction velocity is found to be (*a*) proportional to the concentration of oxalate, (*b*) proportional to the square root of the concentration of iodine, (*c*) inversely proportional to the concentration of KI, and (*d*) proportional to the square root of the incident light intensity. When the absorption is strong (*a*), (*c*), and (*d*) still apply, but the velocity is now *inversely* proportional to the square root of the iodine concentration. The apparent order thus varies between 0·5 and —0·5, according to the extinction. More recently Berthoud (*Trans. Faraday Soc.*, **21**, 554, 1926) cites examples in which the order with respect to the absorbing reactant is 1·5. Such are the additions of bromine to cinnamic acid and to stilbene; in both cases the velocity is given by

$$\frac{dx}{dt} = kI_0^{\frac{1}{2}}[\mathrm{Br_2}] \text{ for strong absorption,}$$

and

$$\frac{dx}{dt} = kI_0^{\frac{1}{2}}[\mathrm{Br_2}]^{1\cdot 5} \text{ for weak absorption.}$$

In all these examples, it will be observed that the absorbing molecule is a halogen and that the velocity is proportional to the *square root* of the incident light intensity. The explanation advanced to account for the reaction course is, in all cases, a primary dissociation of the absorbing halogen into atoms, and this hypothesis appears to be very well supported by the data for the reaction between hydrogen and bromine, and especially by comparison of the velocities in the dark and photochemically (cf. pp. 463 *et seq.*).

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* We mean by "true order" the order of reaction when the light absorption is weak. Under such conditions, the system is practically homogeneous with respect to the (monochromatic) radiation, and the case is theoretically simpler than when the absorption is strong.

Before the application of the quantum theory to photochemistry, two different formulations of photochemical kinetics existed. According to one of these, the "intensity" formulation, the velocity of photochemical reactions is given in terms of an equation of the same form as that for thermal reactions, $\frac{dx}{dt} = Kc_1^{n_1}c_2^{n_2} \ldots$, with the addition that the constant K is a function of the incident light intensity, in general proportional to the light intensity. Thus, the equation

$$\frac{dx}{dt} = kIc_1^{n_1}c_2^{n_2} \ldots \qquad (7)$$

was regarded as applicable to photo-reactions. This view would appear to have been first applied by Wittwer (*Poggendorff's Annalen*, **94,** 597, 1853), the reaction being the photo-decomposition of chlorine-water. The same standpoint was adopted by Nernst (*Lehrbuch*, 5th Edition) and has been called the Nernst-Wittwer "intensity" formulation. Doubts were raised by Wildermann (*Z. physikal. Chem.*, **41,** 88, 1902) as to the general validity of the "intensity" view; he suggested instead that photochemical reaction velocity might be subject to a law analogous to Faraday's Laws of Electrolysis, i.e. the velocity might be determined solely by the amount of radiant energy absorbed. His own experimental work, however, led him to decide in favour of the "intensity" formulation. In 1904 van't Hoff expressed himself in favour of the alternative view, the "absorption" formulation, viz. proportionality between rate of reaction and rate of energy absorption, and Luther and Weigert (*Z. physikal. Chem.*, **51,** 297, 1905) applied this formulation to the treatment of their experimental data on the photopolymerisation of anthracene. It was early recognised that for "unimolecular" reactions the two formulations yield identical results, and we have seen that most photochemical processes have a true order of 1, and an apparent order between 0 and 1. Gros (*Z. physikal. Chem.*, **37,** 176, 1901), who was the first to apply mathematical treatment to the diminution of light intensity with increasing penetration into the reacting system, derived the following equation on the basis of the "intensity" formulation:—

$$\frac{dx}{dt} = k \, . \, \frac{c^{n-1} \, . \, I_0}{\log_e m}(m^{cd} - 1) \qquad (8)$$

In this equation, k is a constant dependent on the temperature; $c =$ concentration of light-sensitive substance; $n =$ reaction order; $I_0 =$ incident light intensity; $d =$ thickness of layer; and $m =$ molecular transparency, defined by $I = I_0 m^{cd}$. When $n = 1$ we have

$$\frac{dx}{dt} = \frac{kI_0}{\log_e m}(m^{cd} - 1), \text{ or } \frac{dx}{dt} = k_1 I_0(m^{cd} - 1).$$

Goldberg (*Z. wiss. Phot.*, **4**, 96, 1906) showed that an identical equation is obtained on the basis of the " absorption " view. He obtained

$$-\frac{dc}{dt}=\frac{kI_0q}{V}(1-m^{cd}).$$

Taking q and V as constants, we have

$$-\frac{dc}{dt}=k_1I_0(1-m^{cd}),$$

identical with Gros's formula when $n=1$.

For a " bimolecular " reaction course, the differential equation for the velocity becomes

$$-\frac{dc}{dt}=k\,.\,\frac{q}{V}\,.\,c^2\,.\,I_x \quad \text{(" intensity " formulation)},$$

where I_x is the light intensity at a point distant x cm. from the place of entry of the light beam.

Writing $$I_x=I_0m^{cx},$$

we obtain for the integrated velocity over the thickness d of the cell

$$-\frac{dc}{dt}=\frac{kqI_0c}{V\log_e m}(m^{cd}-1),$$

and when the reaction vessel is a parallelopiped completely illuminated,

$$-\frac{dc}{dt}=\frac{kI_0c}{d\,.\,log_e\,m}(m^{cd}-1) \quad . \quad . \quad . \quad (9)$$

This equation cannot be integrated, and in order to test whether a reaction follows a bimolecular course it must be applied in its differential form, as was done by Boll (*Compt. rend.*, **156**, 691, 1913), who obtained excellent agreement for the photochemical hydrolysis of the chloroplatinic acids.

In the light of modern views, neither the " intensity " nor the " absorption " formulation can be accounted a satisfactory generalisation of photochemical reaction velocity. Both give equations which may be regarded as extreme cases of the application of the more general principles of the quantum theory. According to the latter, the kinetics of a given photochemical process can only be satisfactorily worked out on the basis of a set of consecutive part-processes, of which all photochemical reactions consist. The kinetic equation which is then obtained depends on the type of mechanism which is assumed, but is in all cases of a more complicated type than that given by either the " intensity " or the " absorption " formulation. Under certain conditions, however, justifiable approximations may be introduced which will yield an equation identical with that derived on the basis of one or other of the older generalisations. To illustrate this, we may take as an example a type of mechanism previously quoted, which is of the simplest possible nature. We assume the process to be dependent on the relative speeds of the three consecutive reactions

$$\begin{aligned}
&(1)\ AB + h\nu \rightarrow AB^* \ldots\ldots\ k_1\\
&(2)\ AB^* \rightarrow AB \ldots\ldots\ k_2\\
&(3)\ AB^* + C \rightarrow \text{Resultants} \ldots\ k_3.
\end{aligned}$$

Here AB is an absorbing molecular species, C a non-absorbing reactant. We then have

$$+\frac{d[AB^*]}{dt} = k_1 I_0[AB] \quad \text{(for the case of weak absorption)}$$

and

$$-\frac{d[AB^*]}{dt} = k_2[AB^*] + k_3[AB^*][C].$$

At the steady state

$$+\frac{d[AB^*]}{dt} = -\frac{d[AB^*]}{dt},$$

and thus $$k_1 I_0[AB] = [AB^*]\{k_2 + k_3[C]\}$$

or $$[AB^*] = \frac{k_1 I_0[AB]}{k_2 + k_3[C]}.$$

The velocity of the measured process (3) is given by

$$\begin{aligned}
\frac{dx}{dt} &= k_3[AB^*][C]\\
&= \frac{k_3 k_1 I_0[AB][C]}{k_2 + k_3[C]} \quad . \quad . \quad . \quad (10)
\end{aligned}$$

If $k_3[C] \gg k_2$, then $\frac{dx}{dt} = k_1 I_0[AB]$, which is the kinetic equation which would be derived from the " absorption " formulation for the case of weak absorption, since $I_0[AB]$ is proportional to the energy absorbed. When $k_3[C] \ll k_2$, then $\frac{dx}{dt} = \frac{k_1 k_3}{k_2} \cdot I_0[AB][C]$, an equation of a type similar to that given by the " intensity " formulation. Dependent on the relative speeds of reactions (2) and (3), therefore, a reaction of the above type might satisfy the predictions either of the " intensity " or of the " absorption " formulation, or, if the terms in the denominator of equation (10) are of the same order of magnitude, might satisfy neither. Recent work goes to show that many photochemical processes follow a more complicated course than the one just assumed, and that therefore it is not feasible to classify such processes in a manner similar to that adopted for dark reactions. Rather, we must recognise that each photochemical reaction involves a primary process whose velocity is determined by the rate of energy absorption, and that this is followed by two or more consecutive " dark " reactions involving activated molecules or atoms. The kinetic equation obtained for the net process will frequently contain concentration terms in both numerator and denominator, but will sometimes permit of conversion into a simpler form.

LIGHT INTENSITY AND REACTION VELOCITY.

It follows from the preceding Section that the velocity of the primary process in photochemical reactions is given by $\frac{dx}{dt}=kI_0(1-e^{-acd})$, and is thus strictly proportional to the incident light intensity I_0 when monochromatic light is employed. For the *total* reaction with monochromatic light,* the same proportionality is also the normal behaviour, though not many quantitative experiments have been carried out to determine over what limits of intensity and to what degree of exactness this relationship holds. Among others, reactions in which direct proportionality between incident light intensity and reaction velocity has been experimentally verified are the photopolymerisation of anthracene in its initial stages (Luther and Weigert, *Z. physikal. Chem.*, **51,** 297, 1905), the chlorine-sensitised decomposition of ozone (Weigert, *Z. Elektrochem.*, **14,** 591, 1908), the decomposition of gaseous chlorine monoxide (Bowen, *J.C.S.*, **123,** 2328, 1923), the decomposition of potassium cobaltioxalate (Vranek, *Z. Elektrochem.*, **23,** 336, 1917), and the decomposition of uranyl formate (Hatt, *Z. physikal. Chem.*, **92,** 513, 1918). In testing the first, second, and fourth of these cases, the alteration in light intensity was effected by variation of the distance of the light source from the illuminated system, and only a four or five fold variation in intensity was tested. A similar variation in light intensity was also used in the third of the above cases, but was obtained by the use of a rotating sector. In the last example quoted—the photochemical decomposition of uranyl formate—a much greater range of intensities was employed, between 200 and 500,000 Lux, and in the initial stages of the reaction direct proportionality between intensity and velocity was found between these limits.

In those photochemical reactions of bromine and iodine whose velocity is proportional to the square root or to the three-halved power of the concentration of halogen, it is found that the rate of reaction is proportional to the square root of the incident light intensity. This relation has been experimentally confirmed by Berthoud and Bellenot (*Helv. Chim. Acta*, **7,** 304, 1924) in the case of the photochemical reaction between iodine and potassium oxalate in aqueous solution:

$$K_2C_2O_4 + I_2 \rightarrow 2CO_2 + 2KI.$$

In order to vary the light intensity, these workers placed between the source of light and the reaction vessel a large opaque disc which was rotated and out of which had been cut sectors of equal magnitude. By using discs from which 2, 4, and 8 sectors had been removed, *mean* light intensities in the ratio 1 : 2 : 4 were obtained. As has been pointed out by Allmand (*Trans. Faraday Soc.*, **21,** 586, 1926), however, this method of intermittent illumination with light of constant intensity is not well adapted to the determination of the effect of variation of intensity on photochemical reaction rate. It simply tests the effect of time of exposure to a constant intensity. As, however, Berthoud and Bellenot's interpretation of their results has since been confirmed by another method, and as their work is of considerable interest and importance, it is not out of place here to reproduce some of their figures. In the first place, the reaction velocity using a given number of sector openings was found to be independent of the speed of rotation, provided that the time between two successive illuminations was less than 0·2 second. It was concluded that after exposure to light the chemical reaction continued for an appreciable period after the light is cut off, and also that if the speed of rotation of the disc were reduced below a limiting value the reaction velocity should decrease. The anticipated falling off in velocity was observed, but the authors did not obtain the expected reaction speed when the disc was rotated very slowly. Experiments using blue light and red light were carried out, and the table shows that the velocity is in both cases proportional not to the number of sector openings but to the square root of this number.

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* For photochemical reaction velocity in non-homogeneous light, see p. 414.

TABLE XXXVIII.

PHOTOCHEMICAL REACTION BETWEEN I_2 AND $K_2C_2O_4$ (BERTHOUD AND BELLENOT).

Number of Sectors.	*k*.	Ratio of Constants (Observed).	Ratio of Constants (Calculated).
Blue Light.			
2	0·00904	1·46	1·41
4	0·0132	2·01	2·00
8	0·0184	1·39	1·41
Red Light.			
2	0·0281	1·44	1·41
4	0·0407	2·01	2·00
8	0·0565	1·39	1·41

The values given in the second column are the velocity constants based on the kinetic equations which are found to reproduce the dependence of the reaction velocity on the concentrations of reactants in blue light and in red light (cf. p. 451).

A thorough re-investigation of the effect of light intensity on this reaction has recently been carried out by Briers, Chapman, and Walters (*J.C.S.*, **129,** 562, 1926), with the result that Berthoud and Bellenot's claim that the square root of the light intensity determines the velocity is substantiated. The method here employed for varying the intensity of the light was as follows. Two lamps were placed side by side and symmetrically situated with respect to the reaction vessel. The latter was exposed for a given time to the light emitted from one lamp, and then for an equal time to the light of the second lamp. The extent of reaction was compared to that effected by both lamps operating for half the total time taken in the two first exposures. It was found that the photochemical change produced in the first experiment was 1·32 times that in the second; the theoretical result based on the assumption of proportionality between velocity and square root of light intensity is 1·41. The slight deviation from the theoretical result is attributed to errors inherent in the nature of the experimental arrangement. It may be taken as satisfactorily established that the reaction under discussion is one whose velocity is proportional to a power of the incident light intensity in the neighbourhood of 0·5.

The same $I^{\frac{1}{2}}$ relationship also applies, according to Berthoud (*Trans. Faraday Soc.*, **21,** 554, 1926), to the photochemical addition of bromine to cinnamic acid, to stilbene, and to α-phenylcinnamonitrile, as well as to the reversal of the last reaction. The $I^{\frac{1}{2}}$ relation is also implicit in the experimental results of Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, **114,** 208, 1924) on the rate of photochemical synthesis of HBr. They found that the reaction velocity is proportional to the square root of the rate of absorption of energy, and though no direct tests of the effect of variation of intensity were carried out, the result implies proportionality between rate of reaction and $I^{\frac{1}{2}}$. According to Bodenstein (*Trans. Faraday Soc.*, **21,** 525, 1926), another reaction in which the square root of the energy absorbed determines the velocity is the photochemical formation of phosgene from CO and Cl_2. It has also been suggested that in the complete absence of oxygen the hydrogen-chlorine reaction would exhibit the same behaviour (see Chapter X.).

Other reactions are known in which the ratio $\frac{\text{velocity}}{\text{incident intensity}}$ decreases with increasing intensity, though no definite mathematical relation such as the $I^{\frac{1}{2}}$ relation is suggested. Some of these cases are heterogeneous reactions for which, with high intensities of illumination, the rate of reaction is limited by the rate of diffusion of a reactant to the illuminated surface. Possibly an example of this, though a very complicated one, is the photosynthetic process in plants. The rate of photo-assimilation depends on a variety of factors, among which are the frequency and intensity of the light, the concentration of carbon dioxide in the medium surrounding the plant, the temperature, and the amount and nature of the chlorophyll available in the plant. If the remaining factors are all of such magnitude as to favour high synthetic activity, then, for low values of the light intensity, photosynthesis is proportional to light intensity. With higher values of the light intensity, however, an increase in this variable causes a less than proportional increase in reaction rate owing to deficiency in the action of one of the other factors. Such behaviour has been experimentally investigated by O. Warburg (*Biochem. Z.*, **100,** 255, 1919) and by Harder (*Jahrb. wiss. Bot.*, **60,** 531, 1921).

In a recent paper (*Trans. Faraday Soc.*, **21,** 459, 1926), Winther draws attention to cases in which a similar effect of variation of light intensity is obtained, but whose explanation is apparently not due to exhaustion phenomena. Such cases are the decomposition of ozone by ultra-violet light, the decomposition of H_2O_2, and the oxidation of HI in aqueous solution by dissolved oxygen. Warburg (*Sitzungsber. Preuss. Akad. Berlin*, p. 644, 1913) found that in "moist" ozonised oxygen of high ozone content the quantum sensitivity of the photochemical decomposition decreases with increasing intensity of the incident light. This result implies that with increasing intensity the ratio $\frac{\text{velocity}}{\text{intensity}}$ diminishes. Comparison of experiments (*a*) and (*b*) and of (*c*) and (*d*) in the table shows this effect.

Experiment.	$\lambda (\mu\mu)$.	Per Cent. O_3 (by Volume.)	A.	$E \cdot 10^6$.	$\phi \cdot 10^5$.
(*a*) . .	253	2·49	0·97	602	1·97
(*b*) . .	253	2·23	0·97	230	2·77
(*c*) . .	287	7·93	0·93	929	3·90
(*d*) . .	283	8·15	0·96	300	6·70

In the table A = fraction of the incident light which is absorbed, E = the absorbed radiation (cal.) per second, and ϕ = number of gram-molecules of ozone decomposed per calorie of absorbed radiation. Since in both pairs comparison is made with approximately equal ozone concentrations present, the change of the quantum sensitivity is due to the different light intensities, which are nearly proportional to the values of E. The evidence in the case of the photochemical decomposition of hydrogen peroxide is not so certain. Tian (*Ann. Physique*, (9), **5,** 248, 1916) found that the reaction velocity is proportional to the intensity. Winther (*loc. cit.*), however, compares the quantum yield of 43·2 obtained by Kornfeld (*Z. wiss. Phot.*, **21,** 66, 1921) employing a solution of concentration 0·049 N and radiation of wave-length 311 $\mu\mu$ with the much smaller quantum yield of 2·9, extrapolated for the same concentration and wave-length from the experiments of Henri and Wurmser (*Compt. rend.*, **157,** 126, 1913). The latter investigators used a much more intense source of radiation than did the former, so that if the two experiments are truly comparable in respect of other factors (such as acidity) which influence the velocity of the process, it must be concluded that proportionality between intensity and reaction rate is not obtained. Comparison of two sets of results obtained by Henri and Wurmser may also be taken as supporting this view, although a different interpretation is possible. Using mixed ultra-violet light of weak intensity and of wave-length between 214 and 298 $\mu\mu$, a high quantum yield for this reaction of 130 was obtained, but with monochromatic light within the same wave-length limits but of greater intensity, the quantum yield was diminished to 5. The photochemical oxidation of HI was studied by Winther (*Z. physikal. Chem.*, **108**, 236, 1924). The reaction is of complex nature, is sensitised by I_3' ions, and is accompanied by a "dark" reaction. Winther finds, however, that the velocity of photochemical oxidation with monochromatic light of wave-lengths in the range 436 — 254 $\mu\mu$ increases with increasing intensity for small values of the latter, but beyond a certain limiting value of the intensity further increase produces no effect on the reaction velocity. Winther rejects the hypothesis that these results are due to impoverishment of oxygen in the illuminated portion of the solution when the light intensity is high. He interprets the decrease in the ratio velocity : intensity with increasing intensity by assuming that double excitation of absorbing I_3' ions is possible (i.e. with high intensities an I_3' ion may absorb two or more quanta), and that I_3' ions which have absorbed a single quantum are alone capable of initiating the reaction. It would seem, however, unless the life of an activated I_3' ion is abnormally great, that the probability of a double excitation of the ion is too small to permit of this hypothesis being applicable. It is further to be noted that, according to Berthoud (see p. 610), the $I^{\frac{1}{2}}$ relation holds for the photochemical oxidation of HI, in which case this reaction falls into line with the other halogen reactions mentioned on p. 409. The explanation of the observed effects of light intensity on the two other processes—decompositions of H_2O_2 and O_3—cannot yet be given; they are somewhat complex processes whose velocities depend on a variety of factors, and further work is necessary before discussion can usefully be attempted. In both cases, however, it does not appear unlikely that the explanation is essentially similar to that in the cases of the halogen reactions following the $I^{\frac{1}{2}}$ relationship, and depends on the assumption of primary dissociation of the absorbing molecule (see Chapter VIII.).

On the other hand, reactions in which the velocity increases more than proportionally to the intensity are much fewer. Baly and Barker (*J.C.S.*, **119**, 653, 1921) have claimed that the velocity of combination of hydrogen and chlorine in light is not in direct ratio to the light intensity as found by Draper (*Phil. Mag.* [iii.], **23**, 401, 1843), but that the ratio $\frac{\text{velocity}}{\text{intensity}}$ increases with increasing intensity. Subsequent investigations have, however, not confirmed this result; it has been established (cf. p. 522) that reaction rate and light intensity are practically proportional. A type of reaction for which the effect under discussion has been established is the destruction of certain fluorescing dyes such as fluorescein and eosin in aqueous solution. The influence of light intensity on the rate of destruction of the fluorescing substance has been determined by Perrin (*Ann. Physique*, (9), **10**, 133, 1918; **11**, 5, 1919) and Wood (*Proc. Roy. Soc.*, **99**A, 362, 1921; *Phil. Mag.*, [vi.], **43**, 757, 1922). The latter exposed two cells of the same depth and containing eosin solutions of the same concentration to strong illumination. One cell was exposed to direct sunlight, the other to sunlight concentrated by a six-inch lens. In both cases the same amount of light was passed in; in one, however, it was spread uniformly over the whole surface area of the cell, in the other it was concentrated on an area of small size. It was found that the solution receiving the very concentrated illumination was decomposed to a much greater extent than that illuminated by normal sunlight. A similar effect of light intensity has been noted by P. Pringsheim (*Z. Physik*, **10**, 176, 1922) on solutions of sodium fluorescein. The interpretation of these results is not clear. Apparently, very high light intensities are necessary for the change, as also, according to Weigert (*Z. Physik*, **10**, 350, 1922), is the presence of oxygen or an oxidising agent. The latter found however (*Nernst Festschrift*, p. 464, 1912) that, although oxygen is required for the change, an increase in the partial pressure of oxygen is attended by a diminution in the reaction velocity, and thus there exists an optimum oxygen concentration of low value. He interprets the abnormally great effect of very strong light intensities as due to the rapid attainment in the illuminated portion of the solution of a small oxygen concentration, the value of which is near the optimum, and which remains constant owing to the slow influx of fresh oxygen by diffusion. Pringsheim (*Z. Physik*, **16**, 71, 1923) criticises this explanation and substitutes in its stead the hypothesis that, for these reactions requiring very strong illumination, the mechanism involves the collision of *two* light-activated molecules; the probability of reaction would then increase with increase in density of activating light. Alternatively might be postulated absorption of more than one quantum by a reacting molecule; if this be the explanation it is not necessary that the quanta be of different sizes, since Pringsheim showed that the reaction occurs on illumination with monochromatic light.

Summing up, we may say that in so far as it has been tested, the velocity of most photochemical reactions is found to be proportional to the incident light intensity. In the case of certain reactions involving a halogen, the velocity varies as the square root of the rate of absorption or of the incident light intensity, and satisfactory mechanisms may be adduced in explanation of this. In the few remaining cases in which the effect of strong intensities is definitely greater or less than direct proportionality, various hypotheses may be brought forward to account for the observed results, but, in general, experimental support of such hypotheses is as yet meagre. The generally suspected cause of a diminishing ratio $\frac{\text{velocity}}{\text{intensity}}$ with increasing intensity is impoverishment of a reactant in the illuminated portion of the reaction system. The cause of the opposite effect, definitely established only for the destruction of dyes in solution, *may be* that the molecule to be activated in such cases require double activation. Further discussion of the effect of light intensity on photochemical change will be found in the papers of Winther (*loc. cit.*) and of Rideal (*Trans. Faraday Soc.*, **21,** 655, 1926).

Actinometry.—The use of actinometers is based on the assumption of direct proportionality between light intensity and reaction velocity; determination of the extent of chemical change in an actinometer may thus under certain conditions afford a measure of the incident light intensity. Among the photochemical reactions which have been described as suitable for actinometric purposes, the following are the most important:—

(*a*) the combination of hydrogen and chlorine (Bunsen and Roscoe, *Pogg. Ann.*, **96,** 373, 1855; **100,** 32, 481, 1857; **101,** 193, 1859);

(*b*) the blackening of silver chloride paper (Bunsen and Roscoe, *ibid.*, **117,** 576, 1862);

(*c*) the liberation of iodine from acidified solutions of potassium iodide (Smith, *Phot. News*, p. 291, 1880);

(*d*) the reaction between mercuric chloride and ammonium oxalate in aqueous solution (Eder's Solution) (*Eder's Handbuch*, Vol. **1**, Part 2, 163);

(*e*) the decomposition of oxalic acid in aqueous solution sensitised by uranyl sulphate (Anderson and Robinson, *J. Amer. Chem. Soc.*, **47,** 718, 1924).

The extent of reaction is followed in (*a*) by measurement of the volume change, in (*c*) by titration of the liberated iodine with sodium thiosulphate, in (*d*) by determination of the weight of precipitated calomel, and in (*e*) by titration of the remaining oxalic acid with potassium permanganate. Bunsen and Roscoe confirmed the so-called *Reciprocity Law* by experiments on reactions (*a*) and (*b*). This law states that the time necessary to produce a given photochemical effect is inversely proportional to the intensity of illumination, i.e. $I \, . \, t =$ constant. It is clear, however, that many factors may operate to limit the applicability of this law. It is unnecessary at present to enumerate all the possible causes of deviations, but it may be mentioned that the well-known experimental arrangement adopted by Roscoe and Bunsen and by many subsequent workers in the case of the hydrogen-chlorine reaction does do away with one disturbing factor, viz. change in the concentrations of reactants during the illumination. In this actinometer, the mixture of the two gases is contained in a glass vessel containing water saturated with the gases. The hydrochloric acid formed on insolation is rapidly absorbed by the water, and the contraction of volume is registered on a narrow horizontal index tube with attached scale and containing water. Sensitive hydrogen-chlorine actinometers of such a type have been used by Burgess and Chapman (*J.C.S.*, **89,** 1407, 1906) and by M. C. C. Chapman (*ibid.*, **123,** 3062, 1923) in their investigations of the kinetics of the reaction.

The importance of actinometers of such a type was formerly much greater than at present, and it is clear that their usefulness is strictly limited. In modern photochemical work they have been almost entirely replaced by absolute physical methods (bolometer or thermopile) for the determination of radiant energy, in spite of the experimental difficulties and inconveniences attached to these methods. Even when the actinometric reaction is unattended by complications and the reaction velocity in homogeneous light is strictly proportional to the intensity over the desired range, the use of the actinometer in exact work is confined to estimations of the relative intensities of monochromatic light. In non-homogeneous light containing frequencies covering a wide range, we may postulate that the action of the mixed light is equal to the sum of the effects of the individual rays (cf. p. 415). The reaction velocity will then be given by an equation of the type

$$\frac{dx}{dt} = \Sigma k I_0 (1 - e^{-\alpha S c}).$$

In this equation c = concentration of the absorbing substance, α = absorption coefficient, and k = photochemical reaction velocity constant and may be a composite term containing concentrations. In general, however, the values of both α and k vary with the wavelength. If the total light intensity be altered, the actinometer will register a correct indication only if the intensities of *all* rays are modified in the same proportion, such for example as would be obtained by change of distance between light source and actinometer. Alteration of total intensity by methods such as increase of wattage of a lamp (which alters the spectral distribution of energy) will not be correctly measured by a chemical actinometer. As already stated, therefore, for exact work actinometers may be used with monochromatic light, but here relative intensities may be as conveniently determined by photometric means. On the other hand, actinometers may be used for yielding approximately correct relative values of the radiation comprised within the spectral region which is strongly absorbed by the photosensitive substance of the actinometer.

REACTION VELOCITY IN NON-HOMOGENEOUS LIGHT.

The treatment of reaction kinetics above given applies only to reactions proceeding under the influence of monochromatic light, though it is to be admitted that in many of the examples cited in illustration, the light employed was far from being monochromatic. As already mentioned, in all photochemical investigations the degree of monochromatism employed has not been specially high, and this is necessarily so, since otherwise accurately determinable yields could not be obtained in a reasonable time. Yet in much photochemical work the activating light has embraced wide spectral ranges—much greater than necessitated by considerations of yield-time ratio—and it is of interest to enquire if the kinetics of such reactions are amenable to mathematical treatment, and in particular to ask how the velocity depends on the total intensity of the mixed light. Only a very incomplete solution of either problem is, however, possible from a theoretical standpoint, and the second question merits further experimental investigation.

We shall first deal with these questions from a formal standpoint, considering only the case for which the reaction velocity in monochromatic light depends solely on the rate of absorption of energy. We assume that the same is true for each activating frequency present in the mixed light and also that the effect of each frequency may be classed as a separate reaction, so that at any point in the system the instantaneous velocity with mixed light is the sum of the instantaneous velocities which would be obtained if the individual frequencies had been separately employed and the concentration of absorbing reactant been the same. With mixed light, therefore, but otherwise with the same conditions as on p. 398, we obtain, instead of equation (3), the equation

$$V dx = q dt \,.\, \Sigma k I_0 (1 - e^{-\alpha S c}) \quad . \quad . \quad . \quad (11)$$

for the velocity of reaction. Here it is to be understood that each of the terms I_0 (incident intensity), k (velocity coefficient), and α (absorption coefficient) in general varies with the wave-length. Integration of this equation with respect to t is not possible, but the following general results are obtainable from the equation as it stands (cf. Wegscheider, *Z. physikal. Chem.*, **103**, 273, 1923):—

1. If the incident light intensity is varied in such a way that the ratios of the intensities of individual frequencies remain constant, then the instantaneous velocity of reaction is proportional to the total incident light intensity. It does *not* follow, however, that the material transformed in a finite time is proportional to total incident intensity, nor that, starting with the same concentration of photolyte, the time necessary for a given transformation is inversely proportional to the total incident intensity.

2. If k and α are both independent of λ, the velocity becomes proportional to total incident intensity, independent of whether or not the ratios of the individual intensities remain constant. Equation (4) of p. 399 holds, with ΣI_0 substituted for I_0. This case is, however, of limited practical interest, since as a general rule both k and (especially) α vary with λ. The absorption coefficient α is strongly dependent on λ near the maximum of a band, and though k may often be regarded as constant over a limited range of wave-lengths, as a general rule it decreases more or less markedly as λ increases.*

3. If k (but not α) is independent of λ, equation (11) becomes

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* The variation of k with λ is discussed in the next Chapter. There are a few reactions in which k is independent of λ; also, in those reactions which obey Einstein's Law at all frequencies, k is proportional to λ.

$Vdx = qdt \, . \, k\Sigma I_0(1 - e^{-\alpha Sc})$, but little is gained in the way of simplification.

4. The total transformation effected by mixed light in a finite time interval is, in general, smaller than the sum of the separate effects which would be produced by the individual frequencies acting separately and over the same interval of time.* This will be the case when the light is not completely absorbed; for total absorption, under the conditions specified, the two effects may be the same. (They may also be equal when the only absorbing substance present is a sensitiser whose concentration remains constant throughout the experiment; for the case of a sensitiser whose concentration increases with time, the sum of the separate effects of the individual frequencies may even be exceeded by the transformation in mixed light.)

This is as far as theory will carry us for the class of reaction considered, the theory being based on the assumption that reaction in polychromatic light is made up of a number of simultaneous reactions which are independent of each other. The total effect produced by polychromatic light in time intervals such that the concentration of photolyte changes appreciably has been shown to be—even in the simplest photochemical reactions—a very complex integral. It depends on such factors as total light intensity, spectral distribution of energy among the individual frequencies, concentration of photolyte, thickness of layer, absorption coefficients for the different wave-lengths, time, etc. In other types of reactions, additional factors such as concentrations of non-absorbing reactants have to be included. Simplification is usually obtainable, however, by determining "instantaneous velocities," or when the light employed is completely absorbed at all stages of the reaction, or if it happens that the absorption coefficients for all wave-lengths are nearly equal.

Turning now to the experimental side, two types of data obtained with polychromatic light are relevant to the above theoretical discus-

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* This may be demonstrated most easily by considering the case when α is independent of the wave-length. Equation (11) then becomes integrable, and we obtain formulæ (4)-(6) of pp. 399-400, with the term kI_0 replaced by ΣkI_0. Considering the case of weak absorption (Formula (6)) and placing $\frac{\alpha qSt}{V} = \theta$, we now obtain

$$\theta\Sigma kI_0 = \log_e \frac{a}{a - x}$$

or

$$x = a(1 - e^{-\theta\Sigma kI_0}).$$

For values of t (and hence θ) which are not too great, one may expand the exponential into a series, use only the first three terms, and thus obtain

$$x = a[\theta\Sigma kI_0 - \tfrac{1}{2}\theta^2(\Sigma kI_0)^2].$$

If, however, by a similar procedure we sum the effects of the individual frequencies acting separately for the time t, we find for this sum (Σy) the value

$$\Sigma y = a[\theta\Sigma kI_0 - \tfrac{1}{2}\theta^2\Sigma k^2I_0^2].$$

Now $(\Sigma kI_0)^2 > \Sigma k^2I_0^2$, hence $\Sigma y > x$, i.e. the sum of the separate effects of individual frequencies over a finite time is greater than the effect of the mixed light over the same period.

sion. The first is concerned with the relation between reaction velocity (strictly "instantaneous velocity") and total incident intensity, when the variation of intensity is effected in such a manner that the energy distribution throughout the spectral range remains constant.* This relation has been determined in a number of cases, and in most instances, as would be anticipated, direct proportionality between I_0 and reaction velocity obtained. Examples are the combination of H_2 and Cl_2 in visible light (M. C. C. Chapman, *J.C.S.*, **125,** 521, 1924), the decomposition of potassium cobaltioxalate in visible light (Vranek, *Z. Elektrochem.*, **23,** 336, 1917), and the decomposition of uranyl formate in ultra-violet light (Hatt, *Z. physikal. Chem.*, **92,** 513, 1918). So far as we are aware, there is no reason to suspect, for reactions whose velocities are proportional to the intensity in monochromatic light, that direct proportionality between intensity and velocity does not obtain in polychromatic light under the conditions specified. The second type of experimental work is concerned with the ratio between the photochemical yield using complex light and the summed effects of the individual rays. It has been shown above that, in general, owing to the differences in the variations of the concentration of photolyte in the two cases, one would anticipate greater yields in the summation of the action of the individual rays, but that if the light is totally absorbed the two yields may be equal. The latter case seems to have been experimentally realised by Luther and Forbes (*J. Amer. Chem. Soc.*, **31,** 770, 1910) in a study of the photo-oxidation of quinine by chromic acid. The yield in complex light was approximately the same as the sum of the separate yields using the component rays. On the other hand, Plotnikow (*Z. physikal. Chem.*, **103,** 299, 1922), in an investigation of the photo-bromination of cinnamic acid in alcohol and in benzene, obtained smaller yields in polychromatic light than the summed effects of the component rays. He found that, with a yield of 100 in the full light of a uviol lamp, the yield in the same time and in the same units with the yellow light of the lamp was 6·5, with the green 37·9, with the blue 64·6, and with the violet + ultraviolet 49·5, or a total of 158·4, i.e. the summed effect was about one and a half times that of the total radiation of the lamp. As already stated however (p. 403), this is a reaction whose velocity in monochromatic light is—according to Berthoud and Beraneck—proportional not to I_0 but to $\sqrt{I_0}$. If this is the case, Plotnikow's result is explained on grounds quite apart from those dealt with by Wegscheider in the theory just given. For, considering experiments in which the concentration of the absorbing substance (Br_2) is the same, the velocity is proportional to the square root of the absorbed energy. In mixed light therefore,

$$\frac{dx}{dt} = \sqrt{k_1A_1 + k_2A_2 + k_3A_3 + \ldots}$$

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* Naturally, the other experimental conditions—concentration of photolyte, thickness of layer, temperature, etc.—are assumed to remain the same.

where A_1, A_2, A_3 . . . represent energies absorbed from the various spectral regions, and k_1, k_2, k_3 . . . are proportionality constants. On the other hand, the sum of the velocities with these spectral regions acting separately is

$$\frac{d(\Sigma y)}{dt} = \sqrt{k_1 A_1} + \sqrt{k_2 A_2} + \sqrt{k_3 A_3} + \ldots,$$

and it is seen that $\frac{d(\Sigma y)}{dt} > \frac{dx}{dt}$.

Work of similar kind has been carried out by Padoa and Vita (*Gazzetta*, **54,** 147, 1924; *Trans. Faraday Soc.*, **21,** 573, 1926; *Gazzetta*, **56,** 164, 375, 1926; *ibid.*, **57,** 87, 1927; *ibid.*, **58,** 3, 1928), who have obtained some remarkable results. According to these investigators, the summed effect of the component rays of white light is greater than that of the polychromatic light in the oxidation of HI, in the reaction between $FeCl_3$ and oxalic acid (both non-sensitised and sensitised by quinine), in the decomposition of Eder's solution, and in the bromination of cinnamic acid. Large differences were occasionally obtained; thus, in the oxidation of aqueous HI by O_2 the effect of the separate lights was claimed to be 3·17 times the effect of white light. Further, they found for the same reaction that by spectrally decomposing white light and subjecting the system to the action of the spectrum, the rate of reaction was 2·2 times that of white light. They consider that some effect of separation of the individual frequencies is established. The most striking result obtained, however, was that observed in a comparison of the effects of white light and of the same light filtered through an ammoniacal solution of copper sulphate. In spite of the fact that with the filtered light only 47 per cent. of the light energy was available, the amount of HI oxidised exceeded that with white light by 25 per cent. In their study of the bromination of cinnamic acid in CCl_4 and in $CHCl_3$, Padoa and Vita exposed the same solution successively to the different strips of the spectrum and found that the net chemical change depended on the order in which the coloured lights were employed. Greater yields accrued when the lights were applied in order of increasing wavelength than when in the reverse order, though in either case the yields were much greater than those with white light. Finally, they found that the behaviour of the H_2—Cl_2 reaction was entirely opposed to that of the reactions mentioned, greater yields now being obtained in complex light than the sum of the yields with the different parts of the spectrum.

If all these results are well founded, extensions to present-day theories would seem to be required to account for them, as they certainly suggest an "antagonistic" action of certain rays when—and only when—present in complex light. Yet we do not consider that discussion is desirable until the results are more firmly established. It should be borne in mind that the reactions studied by Padoa are complex processes whose velocities are highly dependent on the experimental conditions and whose kinetics have not yet been fully elucidated. It is not impossible that the presence of induction periods or of simultaneous "dark" reactions prevented the possibility of valid comparisons in this work, but apart from this the processes are sufficiently complicated to make caution necessary before fully accepting the experimental results. It might be noted that, according to Berthoud and Nicolet (p. 610), the oxidation of aqueous HI is another process whose velocity is proportional to the square root of the light intensity, and for which, therefore, a greater yield from the sum of the actions of the single rays than from white light is to be anticipated. On the other hand, the results for the H_2—Cl_2 reaction are inexplicable in terms of prevailing theories. Further experimental work on the effect of mixed light is required to confirm or deny Padoa's results, either with (photochemically) simpler reactions or with due regard being paid to all the factors which may influence reaction·velocity.

CHAPTER VIII.

EINSTEIN'S LAW AND PHOTOCHEMICAL REACTION MECHANISM I.

RESULTS OF EXPERIMENTAL INVESTIGATIONS ON EINSTEIN'S LAW.

THE most important application of the quantum theory to photochemistry is embodied in the Stark-Einstein Photochemical Equivalent Law, which in its simplest form postulates equivalence between absorbed quanta and molecules of absorbing substance which react. The theoretical basis of this law was briefly discussed in the last Chapter; we shall now deal with the large and rapidly accumulating experimental investigations on the validity of the law, and, in particular, with the mechanisms which have been suggested for the most important photochemical processes. The development of this latter branch of the subject has been very markedly stimulated by the introduction of the Einstein relation, and photochemical work since 1912 has to a considerable degree concentrated on this field. The most important experimental contributions to the study of the energetics of photochemical reactions are those of E. Warburg,* whose pioneering work in this field is now classical. The notation employed by Warburg is useful in connection with measurements dealing with the experimental verification of Einstein's Law, and may here be reproduced. Warburg defines the *fundamental*† *photochemical equivalent* (p) as the ratio $\dfrac{\text{gram-molecules of substance decomposed}}{\text{gram-calories of radiation absorbed}}$, calculated on the basis of Einstein's Law for a photochemical process which occurs under the influence of monochromatic light of frequency ν (wavelength λ). According to the photo-equivalent relation, the radiant energy which must be absorbed in order that one gram-molecule of a photolyte should decompose is $N_0 h\nu$ ergs, or $N_0 h\nu / 4{\cdot}186 \times 10^7$ cal. (where N_0 is the Avogadro Constant). Substituting the values $N_0 = 6{\cdot}062 \times 10^{23}$ and $h = 6{\cdot}547 \times 10^{-27}$ ergs/sec., this amount of energy is equal to $9{\cdot}481 \times 10^{-11}\ \nu$ cal., and, placing $\nu = c/\lambda$ and expressing λ in microns (μ), the energy in calories which must be absorbed to decompose one gram-molecule is found to be $28{,}443/\lambda$.

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* *Sitzungsber. Preuss. Akad.*, p. 216, 1912; p. 644, 1913; p. 872, 1914; p. 314, 1916; pp. 300, 1228, 1918; p. 960, 1919. A summary of this work is given in *Z. Elektrochem.*, **26**, 54, 1920 (see also, *Z. Electrochem.*, **27**, 133, 1921).

† This is the translation given by Allmand (*Trans. Faraday Soc.*, **21**, 441, 1926) of Warburg's term " indizierte."

$$\text{Hence } p = \frac{\text{gram-molecules decomposed}}{\text{calories absorbed}} = \frac{\lambda}{28443} \ (\lambda \text{ in microns}).$$

According to the direct interpretation of Einstein's Law, therefore, the extent of photochemical decomposition ought to be proportional to the product of absorbed radiant energy and wave-length, and should be independent of all other factors such as concentration and temperature.* Further, for all photochemical processes the quantity p has the same value for identical wave-length of the activating light. The table gives for a few wave-lengths the value of the fundamental photochemical equivalent (p) and of its reciprocal ($1/p$), the number of gram-calories of radiation absorbed per gram-molecule decomposed.†

TABLE XXXIX.

$\lambda(\mu)$.	$p \,.\, 10^5 \frac{\text{moles}}{\text{calories}}$.	$\frac{1}{p} \frac{\text{calories}}{\text{moles}}$.
0·207	0.7286	137,300
0·253	0·8904	112,300
0·282	0·9924	100,800
0·486	1·710	58,470
0·589	2·073	48,240
0·800	2·816	35,510

Let us now denote by ϕ (effective photochemical equivalent) the value of the quotient $\frac{\text{gram-molecules of photolyte decomposed}}{\text{calories of radiation absorbed}}$ obtained *experimentally* in any process effected by monochromatic light. As has been already suggested in the last Chapter, this quantity will not, as a general rule, be equal to the theoretical value p, owing to the fact that all known photochemical processes are complicated by secondary thermal reactions subsequent to the actual primary process caused by the light. The quantum efficiency (γ) of the process is then simply ϕ/p, i.e. the ratio of the number of molecules actually decomposed per unit of absorbed energy to that predicted by Einstein's Law.‡

Most of the experimental work in photochemistry prior to 1913 is not suited to yield information with respect to the ratio between absorbed energy and extent of chemical reaction, although in certain cases approximate conclusions may be arrived at, as was shown by

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* Naturally, in so far as these factors do not influence the absorption.

† Allmand (*loc. cit.*) translates Warburg's term for $1/p$ ("Valenzstrahlung") into equivalent radiant energy, and suggests it be given the name of *Warburg*.

‡ The utility of this nomenclature for photochemical purposes is due to energy terms being expressed in heat units, the form most convenient to chemists. For example, the statement that a substance absorbing light of wave-length 0·253 μ is activated to the extent of 112,300 cal. per mole is in a more convenient form than if the energy were expressed in some other form.

Winther (*Z. wiss. Phot.*, **11,** 92, 1913), Weigert, (*ibid.*, **11,** 381, 1913), and in especial by Bodenstein (*Z. physikal. Chem.*, **85,** 329, 1913; *Z. Elektrochem.*, **19**, 836, 1913). The latter discussed twenty reactions studied by various investigators and, making rough estimates of the amounts of energy absorbed, succeeded in calculating the order of magnitude of the quantum yields. He proved for example that the hydrogen-chlorine reaction is extraordinary light-sensitive, about 10^6 molecules of HCl being formed per quantum absorbed.

Since the date of Bodenstein's paper (1913) many direct measurements of quantum yield in photochemical reactions have been carried out. Such determinations require (*a*) measurements of the extent of reaction, (*b*) determination of the amount of radiant energy absorbed by the photosensitive substance, and (*c*) a reasonable degree of monochromatism of the absorbed radiation in order that the mean value of ν shall not be seriously in error. In the following tables are summarised the results of such investigations in which the absorbed energy has been directly measured. The reactions studied are divided into three classes, (*a*) gaseous reactions, (*b*) liquid reactions, and (*c*) miscellaneous reactions and reactions in solid systems. The first column in the tables gives the photochemical reaction, the second the observer, the third the wave-length of the activating light, and the fourth the value of the quantum efficiency of the process $\left(\gamma = \frac{\phi}{p}\right)$. The value of γ is calculated with respect to the *absorbing* reactant except in the cases of sensitised reactions. The usual formulation of Einstein's Law cannot then apply, as the absorbing constituent remains unchanged; the values of γ given relate to molecules of one of the reacting species decomposed per quantum absorbed by the sensitiser. In using the tables, it is necessary to note that the quantum efficiency of many reactions depends—in some cases markedly—on the experimental conditions; in the last column, some indication is attempted of the conditions under which the quoted value of γ was obtained. These summarising tables are practically reproductions—with a few additions—of the excellent tables drawn up by Allmand (*Trans. Faraday Soc.*, **21,** 438, 1926).

TABLE XL.

GAS REACTIONS.

Reaction.	Observer.	λ(μμ).	γ.	Remarks.
$2HBr \rightarrow H_2 + Br_2$	Warburg[1]	209	2·08	Independent of p_{HBr}, p_{N_2}, or p_{H_2}.
		253	2·00	
$2HI \rightarrow H_2 + I_2$	Warburg[2]	207	1·98	Bodenstein and Lieneweg[3] found a temperature coefficient of unity between $t = 150°$ and $t = 175°$, and that γ is independent of p_{N_2} up to $p_{N_2} = 3·5$ atm.
		253	2·08	
		282	2·06	
$3O_2 \rightarrow 2O_3$	Warburg[4]	207	3·1	$p = 47·5$ atm.
		207	2·9	$p = 125$,,
		207	2·3	$p = 300$,,
		253	1·85	$p = 97$,,
		253	1·75	$p = 125$,,
		253	0·9	$p = 300$,,
$2NH_3 \rightarrow N_2 + 3H_2$	Warburg[5]	209	0·23	γ independent of p_{NH_3}.
Ditto	Kuhn[6]	202·5 — 214	0·4 — 0·5	γ independent of p_{NH_3} between 5 — 900 mm. γ increases with increasing temperature. At $t = 500°$, $\gamma = 3·3$, and decreases with increasing p_{H_2}. It also decreases if the light is made more monochromatic.
$2O_3 \rightarrow 3O_2$	Warburg[7]	253	1·7 in He 1·1 in N_2 0·3 in O_2	For mixtures whose ozone concentration is less than 0·5 per cent. Higher values are obtained with strong ozone concentrations, and γ is increased by water vapour.
$2O_3 \rightarrow 3O_2$	Kistiakowski[8]	620	2·8 — 0·1	γ increases with increasing $[O_3]$ and diminishes with increasing $[O_2]$. Substitution of O_2 by He increases γ.
$2O_3 \rightarrow 3O_2$ (sensitised by Cl_2)	Bonhoeffer[9]	416	2	Reaction velocity independent of $[O_3]$.
$2O_3 \rightarrow 3O_2$ (sensitised by Br_2)	Bonhoeffer[9]	416	30	
$H_2 + Cl_2 \rightarrow 2HCl$	Marshall[10]	300 — 400 (Mean 350)	$10^1 — 3.10^4$	$p_{H_2} \gg p_{Cl_2}$. Values of γ increase with increasing total pressure. Latter varied between 0·01 — 60 mm.

TABLE XL—(*continued*).

Reaction.	Observer.	$\lambda(\mu\mu)$.	γ.	Remarks.
$H_2 + Cl_2 \rightarrow 2HCl$	Kornfeld and Müller[11]	436	$1 . 10^5$	Maximum value obtained. Total pressure = 760 mm; p_{O_2} estimated as 0·08 mm.
Ditto	Porter, Bardwell and Lind[11a]	Mean 410	$7 . 10^4$	Maximum value obtained.
$2Cl_2O \rightarrow 2Cl_2 + O_2$	Bowen[12]	460	2·3	
Ditto	Bodenstein and Kistiakowski[13]	430	2·0	Same yield for direct reaction as for the reaction sensitised by chlorine. γ for $t = 10°$. Temperature coefficient = 1·09.
$2NOCl \rightarrow 2NO + Cl_2$	Bowen & Sharp[14]	500 — 438 (Mean 470)	0·5	
$CO + Cl_2 \rightarrow COCl_2$	Bodenstein[15]	438	1000-1500	γ increases with increasing $[Cl_2]$ and is diminished by drying the reaction mixture.
Ditto	Bonhoeffer[9]	416	2700	1 per cent. O_2 present.
$H_2 + Br_2 \rightarrow 2HBr$	Bodenstein and Lütkemeyer[16]	430	—	See p. 462. γ varies with intensity.
$C_6H_{12} + Br_2 \rightarrow C_6H_{11}Br + HBr$	Nernst & Pusch[17]	476	1·1	
Ditto	Noddack[18]	469	1·0	
$H_2 + O_2 \rightarrow H_2O_2$ (sensitised by Hg)	Marshall[19]	253·6	6·6	$t = 70°$. Maximum experimental value. True value probably greater.
$CO + H_2 \rightarrow H . CHO$ (sensitised by Hg)	Marshall[19]	253·6	6·0	Ditto.
Decomposition of acetaldehyde vapour	Bowen & Watts[20]	313	2	Two reactions occur, (*a*) photolysis into $CH_4 + CO$ and (*b*) polymerisation.
Decomposition of acetone vapour	Bowen & Watts[20]	313	Ca. 2	Reaction products C_2H_6 and CO.
Decomposition of N_2O	Macdonald[53]	186-199 (Mean = 190)	3·9	γ independent of temperature between 0° and 40°; also independent of p_{N_2O}.
Decomposition of NO	Macdonald[53]	186-199 (Mean = 190)	1·5	Chief products of reaction are N_2 and O_2, some N_2O and NO_2 also formed.
Decomposition of azomethane	Ramsperger[54]	Mean = 366	2	γ independent of pressure and temperature.

TABLE XLI.—REACTIONS IN LIQUID SOLUTION.

Reaction.	Observer.	$\lambda(\mu\mu)$.	γ.	Remarks.
$2HI \rightarrow H_2 + I_2$	Bodenstein and Lieneweg [3]	300	1·84	Liquid HI.
$2CCl_3Br + Cl_2 \rightarrow 2CCl_4 + Br_2$ (in CCl_4)	Noddack [18]	410	0·9	Same yield without solvent or with CCl_4 (or $SiCl_4$) as solvent. γ independent of ratio $\frac{SiCl_4}{CCl_3Br}$ or $\frac{CCl_4}{CCl_3Br}$ up to ratio 50 : 1.
Ditto	Grüss [21]	449	0·9	
$2CCl_3Br + O_2 \rightarrow COCl_2 + Br_2 + Cl_2$ (sensitised by Br_2 in CCl_4)	Grüss [21]	436 — 407	0·9	Solutions saturated with O_2 or with air.
$2ClO_2 \rightarrow Cl_2 + 2O_2$ (in CCl_4)	Bowen [22]	445	0·8	γ independent of $[ClO_2]$.
$2Cl_2O \rightarrow 2Cl_2 + O_2$ (in CCl_4)	Bowen [22]	445	0·9	γ independent of $[Cl_2O]$.
Maleic ester → Fumaric ester (sensitised by Br_2 in CCl_4)	Eggert & Borinski [23]	436 546	295 155	$t^\circ = 21$. γ independent of $[Br_2]$ and [Ester]. High temperature coefficient.
Maleic ester + Br_2 → Dibromsuccinic diethyl ester (in CCl_4)	Eggert & Borinski [23]	436 546	8·2 4·1	$t = 21^\circ$. $[Br_2] = 0·1$. γ proportional to $[Br_2]$. High temperature coefficient.
Fumaric ester + Br_2 → Dibromsuccinic diethyl ester (in CCl_4)	Eggert & Borinski [23]	436 546	8·2 4·1	$t = 21^\circ$ $[Br_2] = 0·1$. γ proportional to $[Br_2]$. High temperature coefficient.
$2KNO_3 \rightarrow 2KNO_2 + O_2$ (in H_2O)	Warburg [24]	207 253 282	0·25 0·17 0·024	γ dependent on $[KNO_3]$ and $[H^\cdot]$. Values relate to $[KNO_3] = 0·33$.
Maleic acid → Fumaric acid (in H_2O)	Warburg [25]	207 253 282	0·03 0·04 0·03	Values for 0·01*N* solutions. γ decreases with increasing [Maleic acid].
Fumaric acid → Maleic acid (in H_2O)	Warburg [25]	207 253 282	0·11 0·10 0·13	Values for 0·01*N* solutions. γ increases with increasing [Fumaric acid].
$PtCl_4(OH)_2H_2 + 3H_2O \rightarrow PtCl(OH)_5H_2 + 3HCl$ (in H_2O)	Boll [26]	238 254 310 546	4·2 1·9 0·093 0·0038	Values for concentration of $10^{-4}N$. γ increases with increasing concentration.
$2K_3Co(C_2O_4)_3 \rightarrow 2CoC_2O_4 + 3K_2C_2O_4 + 2CO_2$ (in H_2O)	Vranek [27]	366 405 436	1·5 0·9 0·6	γ independent of concentration (?).

TABLE XLI.—(*continued*).

Reaction.	Observer.	$\lambda(\mu\mu)$.	γ.	Remarks.
$2H_2O_2 \rightarrow 2H_2O + O_2$ (in H_2O)	Henri and Wurmser [28]	214 — 298 (Mean 230)	130	
		208 280	6 4·5	Monochromatic illumination.
$2H_2O_2 \rightarrow 2H_2O + O_2$ (in H_2O)	Kornfeld [29]	311	7 — 80	γ increases with increasing $[H_2O_2]$.
$CH_2Cl . COOH + H_2O \rightarrow CH_2OH . COOH + HCl$	Rudberg [30]	253	1·0	Concentration between 0·5 and 0·3N.
$CH_2Br . COOH + H_2O \rightarrow CH_2OH . COOH + HBr$	Rudberg [30]	253	0·33	Concentration between 0·02 and 0·01N. γ increases with increasing [OH′].
Photolysis of $KMnO_4$ (in H_2O)	Rideal & Norrish [31]	322	0·5	γ increases with increasing $[H_2SO_4]$.
$2Fe^{\cdot\cdot} + I_2 \rightarrow 2Fe^{\cdot\cdot\cdot} + 2I'$	Rideal & Williams [32]	579	1·0	γ with respect to I_2.
Decomposition of oxalic acid (in H_2O)	Anderson and Robinson [33]	200 — 280	0·0009	
Decomposition of oxalic acid sensitised by UO_2SO_4 (in H_2O)	Anderson and Robinson [33]	365	0·028	[Oxalic acid] = 0·01, $[UO_2SO_4]$ = 0·01.
		200 — 280	0·04	[Oxalic acid] = 0·01, $[UO_2SO_4]$ = 0·01.
		200 — 280	0·0022	[Oxalic acid] = 0·01, $[UO_2SO_4]$ = 0·00002.
Decomposition of uranyl oxalate (in H_2O)	Bowen & Watts [20]	313	1	
Ditto	Büchi [34]	420	1	
Decomposition of uranyl formate (in H_2O)	Büchi [34]	420	Ca. 0·7	Hatt [35] previously found $\gamma > 0·4$.
Oxidation of HI by O_2 (sensitised by I_3')	Winther [36]	280 313 366 405 436	6·5 — 70	γ depends on the energy absorbed, increasing as this is decreased.
Chlorination of toluene	Book & Eggert [37]	405	Ca. 27	$t = -80°$.
$o\text{-}C_6H_4(NO_2)CHO \rightarrow o\text{-}C_6H_4(NO)COOH$ (in acetone)	Weigert and Brodmann [38]	366 405 436	0·5	γ independent of concentration.
Allocinnamylidene acetic acid $\rightarrow$ normal form (sensitised by I_2 in $CHCl_3$)	Ghosh & Gupta [39]	Mean 500	1·8	Extrapolated value for high concentrations of allo-acid.
Bromination of cinnamic acid (in CCl_4)	Ghosh and Purkayostha [40]	Mean 470	436	$t = 26°$. High temperature coefficient.
Bromination of stilbene (in CCl_4)	Ghosh and Purkayostha [40]	Mean 470	305	$t = 26°$. High temperature coefficient.
$CH_3 . CO . CH_3 + H_2O \rightarrow CH_4 + CH_3COOH$	Bowen & Watts [20]	313	$< 0·2$	Henri [28] found $\gamma = 1300$ at 298-214 $\mu\mu$ (Mean 230 $\mu\mu$).

Reaction.	Observer.	$\lambda (\mu\mu)$.	γ.	Remarks.
$K_2C_2O_4 + I_2 \rightarrow 2KI + 2CO_2$ (in H_2O)	Berthoud and Bellenot[41]	Mean 486	0·11* 3·2**	* γ with respect to total energy absorbed. ** γ with respect to energy absorbed by I_2. γ depends on intensity of illumination, and temperature. In another paper[42] the figure $\gamma = 25$ for blue light is given.
$2K_2C_2O_4 + I_2 \rightarrow 2KI + CO_2$ (in H_2O)	Mukerji and Dhar[43]	Mean 473	0·46	$t = 30°$.
Sodium potassium tartrate (Rochelle salt) + Br_2 (in H_2O)	Mukerji and Dhar[43]	Mean 473	450	$t = 30°$.
Ferrous sulphate + I_2 (in H_2O)	Mukerji and Dhar[43]	Mean 565 (?)	0·63	
Sodium nitrite + I_2 (in H_2O)	Mukerji and Dhar[43]	Mean 565	0·88	$t = 30°$.
Sodium formate + I_2 (in H_2O)	Mukerji and Dhar[43]	Mean 565	10	$t = 30°$.
Decomposition of $K_3Mn(C_2O_4)_3$ (in H_2O)	Ghosh and Kappanna[44]	Mean 488	1	
Decomposition of oxalic acid (in H_2O)	Allmand & Reeve[50]	248 — 275 (Mean 268)	0·01	Solutions 0·6 — 0·7 *M*.
		280 — 313 (Mean 300)	0·0041	Initial stages of reaction $C_2O_4H_2 \rightarrow H\,.\,COOH + CO_2$.
		365	0·00094	Much higher values for weaker solutions.
Decomposition of formic acid (in H_2O)	Allmand & Reeve[51]	254 — 275 (Mean 260)	2·7	0·11 — 2·4*N* solutions. Two reactions occur :— (*a*) $H\,.\,COOH \rightarrow H_2 + CO_2$ (*b*) $H\,.\,COOH \rightarrow H_2O + CO$.
		280 — 313 (Mean 300)	1·0	
Decomposition of chlorine water and of HClO	Allmand, Cunliffe and Maddison[52]	365 — 405	Ca. 2	γ practically independent of λ between 313 $\mu\mu$ and 436 $\mu\mu$. γ decreases on addition of electrolytes such as HCl, LiCl and Na_2SO_4.
Decomposition of NaOCl	Allmand & Webb[55]	254	4·7	
		313	1·2	γ increased by NaCl.
		365	Ca. 1·0	
Polymerisation of anthracene	Weigert and Jäckh[56]	366 313	0·48	Limiting value at high anthracene concentrations. Solvents—benzene, toluene, xylene.

TABLE XLII.

Reaction in Solids and Miscellaneous Reactions.

Reactions.	Observer.	$\lambda(\mu\mu)$.	γ.	Remarks.
Assimilation of CO_2 in the Alga *Chlorella* (sensitised by chlorophyll)	O. Warburg and Negelein[45]	660 578 436	0·23 0·23 0·20	γ with respect to CO_2.
Decomposition of AgBr (in photographic dry plates)	Eggert and Noddack[46]	365 406 436	1·0	Limiting value for start of reaction and for not too great light intensities.
Decomposition of AgCl in AgCl — gelatine plates	Eggert and Noddack[47]	365	0·9	
Decomposition of AgCl (sensitised by Ag) on printing-out paper	Weigert[48]	436	1	Initial stages of reaction.
$o\text{-}C_6H_4(NO_2)CHO \rightarrow o\text{-}C_6H_4(NO)COOH$	Bowen, Hartley, Scott & Watts[49]	Violet light	Ca. 1	

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It has already been emphasised that Einstein's Law, interpreted in the strict sense of demanding equivalence between molecules decomposed and quanta of radiation absorbed, cannot be generally true for photochemical processes, owing to the effect of secondary "thermal" reactions subsequent to the primary "light" process. The law must be limited to the primary process; as the tables show, the actually observed amount of chemical change may be exactly equivalent to this, it may be some simple multiple—twice or thrice, or it may be much larger or much smaller, depending on the nature and the extent of the secondary processes. The importance of the generalisation is primarily due to two reasons—(*a*) the statement of the rule that absorption occurs in quanta, and (*b*) the basis which this affords for the elucidation of photochemical reaction mechanism. Strong evidence for the validity of (*a*) is afforded by an examination of the experimental data for the reactions given in the tables. Although the actual values of quantum efficiency experimentally determined vary between $9 \cdot 10^{-4}$ and 10^5, about 65 per cent. of the reactions so far investigated show quantum yields approximately equal (within a factor of 3) to those demanded by Einstein's Law (Bowen and Watts, *J.C.S.*, **129,** 1607, 1926). Further, the simple quantitative relations found in such reactions as the photochemical decomposition of hydrobromic and hydriodic acids, and the chlorination of trichlorbrommethane must be regarded as evidence from the chemical side that molecular activation occurs by quantum absorption. Porter, Bardwell, and Lind (*J. Amer. Chem. Soc.*, **48,** 2603, 1926) cite evidence of a somewhat different character in support of Einstein's Photochemical Equivalence Law. They determined the yields of hydrochloric acid formed in identical hydrogen-chlorine mixtures (1) on illumination and (2) through the action of α-rays from radium emanation. The reaction in both cases is extremely sensitive to impurities and the primary yield is obscured by the much larger yield due to secondary reaction. They found, however, that the ratio of HCl molecules formed per ion-pair produced by the action of α-rays to the number formed per quantum absorbed on illumination is constant for all sensitivities over a range of 500-fold. Here, therefore, we have two distinct physical agents, light and α-particles, acting *via* different primary steps, excitation and ionisation, producing total reaction greatly in excess of the unit quantities involved in the primary step, yet the ratio of the yields per unit quantities of action is constant and of the order of unity. This must mean that in a given H_2—Cl_2 mixture the ratio of secondarily produced HCl to that produced by the primary process is the same for both methods of activation, and one concludes "that the ionic relationship lends independent support to the quantic one forming the basis of the photochemical equivalence law."

The primary process, which is in general the formation of an activated molecule, but may in certain cases be the dissociation of a diatomic molecule into its component atoms, thus obeys the Einstein-Stark relationship. What follows afterwards is determined, however, by the nature of the system, its temperature, pressure, and other factors. The methods whereby activated molecules may lose their excess energy have been considered in the previous Chapters; of particular importance from the photochemical standpoint are (*a*) collisions which result in chemical reaction, (*b*) deactivation by non-reactive collision, and (*c*) the nature and extent of the secondary chemical processes. The resultant net effect of the primary and secondary changes may be such as to make impossible any simple relationship between the number of quanta absorbed and molecules reacting; on the other hand, in processes which in general are of a less complicated type, we may find simple stoichiometric relationships, e.g. $\gamma = 1$, 2, or 3, as seen in the tables. The Einstein Law has been of great value in the development of the study of reaction mechanism. By the determination of the quantum sensitivity of a photochemical reaction under different conditions, a rational basis for the formulation of a reaction scheme is obtainable. It must be admitted, however, that our interpretation of the experimental results of the above tables is very largely hypothetical. This is necessarily so, in view of the large number of possibilities of energy transfer and of secondary reactions in photochemical processes. Apart from complications and difficulties of a physical kind, e.g. the uncertain nature of molecular excitation, effects due to solvent or in gaseous systems to high pressures, etc., it is very difficult to obtain direct evidence of the appearance of intermediate products of short life—such as atoms—often postulated in explanation of the reaction course. We must recognise that many of our hypotheses and suggested reaction mechanisms are only provisional; they serve to correlate existing data and to suggest fresh lines of development.

Before proceeding to discuss some of the reactions of Tables XL. and XLI. in more detail, it may be advantageous briefly to set down certain of the conclusions of previous Chapters regarding the consequences of absorption of light by atoms and molecules.

(1) A normal atom which absorbs light of suitable wave-length (line absorption) is converted into an activated atom. Its subsequent fate is conditioned by the nature of the system, temperature, pressure, etc. It may

(α) re-radiate all the same energy at the same frequency,
(β) re-radiate at a lower frequency, with simultaneous conversion into an intermediate state of activation,
(γ) collide with another atom or molecule and transfer its energy without emission of radiation.

The time during which an atom normally remains in an excited state is (in the absence of collisions) about 10^{-8} second. Yet other excited states are known—metastable states—characterised by a life period which, in the absence of disturbing collisions, is infinitely long (cf. Hg in the 2^3P_0 state).

(2) Work on resonance radiation and fluorescence of gases and vapours has yielded important information in respect of "collisions of the second kind"; in particular with regard to the probability of transfer of energy of activation on collision.

(3) In many cases the absorption lines of atoms converge to a limit on the short wave side of the spectrum; beyond this limit, continuous absorption is found. The limiting frequency corresponds to complete elimination of an electron (i.e. ionisation), the continuous region beyond to ejection of the electron with variable amounts of kinetic energy.

(4) The spectra of molecules are more complex and the interpretation of such spectra is but in its initial stages at present. For diatomic molecules we may have as primary process:—

(α) Formation of activated molecules by a change in electron configuration coupled with changes in vibrational and rotational states, such cases yielding band spectra. The activated molecules may re-radiate their excess energy as fluorescence, they may suffer collisions of the second kind, or they may dissociate or react chemically on collision with other molecules.
(β) Dissociation into atoms "in one elementary act." In such cases the absorption spectrum is continuous for wave-

lengths smaller than the convergence limit. The molecule then dissociates, the excess energy being converted into kinetic energy of the separating atoms. In the case of the halogens for example, Frank and others postulate primary dissociation with light of frequency greater than the convergence limit into a normal and an excited atom, the latter because the energy corresponding to this limit is greater than the thermochemical energy required for the formation of two normal atoms. Other cases are NaI, which dissociates into a normal iodine atom and an excited Na atom, and HI and HBr dissociating into H atoms and excited halogen atoms.

(5) The elucidation of the spectra of polyatomic molecules is still less advanced. Apparently, no cases of primary dissociation have so far been encountered (see, however, p. 241) and formation of activated molecules may be regarded as the rule.

In accordance with the above considerations, Gerke (*J. Amer. Chem. Soc.*, **49,** 2071, 1927) has proposed to divide photochemical reactions into two main classes: (A) *Excited molecule* (*or atom*) *reactions*, when the absorbing entity is activated by primary light action, and (B) *primary decomposition reactions*, when light dissociates the absorbing (diatomic) molecule. The former class, he subdivides into (α) *excited reactant* and (β) *excited sensitiser* types, according as to whether the absorbing substance is a stoichiometric reactant or a

TABLE XLIII.

Reaction.	Absorbing Substance.	Type of Spectrum.	Wave-length (Å).
A. EXCITED MOLECULE TYPE.			
(α) *Excited Reactant.*			
$3O_2 \rightarrow 2O_3$	O_2	Band	1970-1756
$2NH_3 \rightarrow N_2 + 3H_2$	NH_3	,, (?)	2260-1515
$2O_3 \rightarrow 3O_2$	O_3	,,	6700, also U.V.
$O_2 + 2CH_3CHO \rightarrow 2CH_3COOH$	CH_3CHO	,,	2800-2350
(β) *Excited Sensitiser.*			
$H_2 \rightarrow 2H$ (and other Hg-sensitised processes)	Hg	Line	2536
$2N_2O_5 \rightarrow 2N_2O_4 + O_2$	$NO_2 - N_2O_4$	Band	4600-4000
B. PRIMARY DECOMPOSITION TYPE.			
$2HCl \rightarrow H_2 + Cl_2$	HCl	Continuous	2640-1800
$2HBr \rightarrow H_2 + Br_2$	HBr	,,	3320-1800
$2HI \rightarrow H_2 + I_2$	HI	,,	2600-1800
$2H_2S \rightarrow 2H_2 + S_2$	H_2S	,,	2300-1800
$CH_3CHO \rightarrow CH_4 + CO$	CH_3CHO	,,	2300-1800
$I_2 \rightarrow I + I^*$	I_2	,,	5000
$Br_2 \rightarrow Br + Br^*$	Br_2	,,	5200
$Cl_2 \rightarrow Cl + Cl^*$	Cl_2	,,	4800
$O_2 \rightarrow 2O$ (also O_3)	O_2	,,	1750

sensitiser. It is seen, therefore, that a given photochemical reaction may belong to the excited molecule type in one region of the spectrum and to the primary decomposition type in another. Table XLIII illustrates the division advocated by Gerke.

PHOTOCHEMICAL REACTIONS IN GASEOUS MEDIA

The Photochemical Decomposition of HBr and HI.—These two reactions are of great interest from a theoretical standpoint. They form cases in which very simple photochemical behaviour is found even with great variations in the experimental conditions, in which the requirements of the photo-equivalent law has been verified with great exactness, and in which the question of reaction mechanism may now be regarded as settled. Considering first the quantum yield in these reactions, this has been determined with great accuracy by E. Warburg (Refs. (1) and (2), p. 429). For the decomposition of hydrobromic acid, the gas was diluted either with hydrogen or with nitrogen, and the mixture swept through a quartz cell exposed to monochromatic ultra-violet light. The bromine in the issuing gas was determined by absorption in potassium iodide solution and titration of the liberated iodine. Experiments were carried out using the two wave-lengths 209 $\mu\mu$ and 253 $\mu\mu$, the absolute amounts of energy absorbed being determined by bolometric measurements. The partial pressure of HBr in the gas mixture was also varied. Employing light of 209 $\mu\mu$, the value of ϕ was found to be $1{\cdot}53 \times 10^{-5}$ moles HBr decomposed per calorie of radiation absorbed, and was the same whether H_2 or N_2 was the diluent. At the longer wave-length, ϕ was found to be $1{\cdot}79 \times 10^{-5}$. These values are nearly double the values (p) calculated on the basis of Einstein's Law for these wave-lengths ($0{\cdot}73 \times 10^{-5}$ and $0{\cdot}89 \times 10^{-5}$), showing that two molecules of HBr are decomposed per quantum absorbed ($\gamma = 2$).

For the photolysis of hydriodic acid, it was found possible to carry out experiments with light of three wave-lengths, viz., 207, 253, and 282 $\mu\mu$, and the reaction serves as a still better test of Einstein's Law. The same experimental method as in the case of HBr decomposition was used. Mixtures of HI and H_2 were employed and the partial pressure of the former varied between 80 and 300 mm. Hg. Table XLIV reproduces the results obtained using light of wave-length 207 $\mu\mu$, and shows the accuracy attainable in such measurements in which very small yields of product are determined.

The mean values of $\phi \,.\, 10^5$ at the three wave-lengths 207, 253, and 282 $\mu\mu$ were found to be 1·44, 1·85, and 2·08 respectively, which values are again—within the experimental error—double the values calculated from Einstein's Law, 0·73, 0·89, and 0·99. The results are thus analogous to those with HBr; at each wave-length, two molecules of HI are decomposed per quantum absorbed.

Bodenstein and Lieneweg (Ref. (3), p. 429) have shown that in the case of the photochemical decomposition of HI, the same quantum sensitivity persists even on drastic alteration of the experimental conditions. They observed that the reaction velocity was independent

TABLE XLIV.

Photochemical Decomposition of HI (Warburg).

$\lambda = 207\ \mu\mu$.

p_{HI}	A.	$E \times 10^6$.	$\phi \times 10^5$.
82·4	0·980	318	1·44
88·3	0·997	342	1·44
112·7	0·993	362	1·35
112·7	0·990	327	1·54
83·9	0·983	297	1·37
80·2	0·967	360	1·43
86·9	0·984	313	1·48
		Mean	1·44

of the concentration of the indifferent gas nitrogen (tested up to pressures of 3·5 atmospheres) and that change of temperature between 150° and 175° had no effect on the photochemical rate. Further, greatly increasing the concentration of HI by liquefaction did not change the quantum sensitivity; with light of 300 $\mu\mu$ and liquid HI the value $\gamma = 1{\cdot}84$ was obtained, which agrees well with Warburg's value of 2. They have further shown that the reaction is not sensitised by iodine.

Reaction Mechanism.—Two alternative formulations may be employed to explain the quantum yield of 2 found experimentally in these reactions. The first is that of Warburg, who assumed that the primary process is the dissociation of the halogen acid into atoms. Taking the case of HI decomposition (the HBr reaction is exactly analogous) the postulated primary process is

$$(1)\ \mathrm{HI} + h\nu \rightarrow \mathrm{H} + \mathrm{I}.$$

There is then the possibility of the reactive atoms thus formed reacting further, according to

$$\begin{array}{lll} (2) & \mathrm{H} + \mathrm{HI} & \rightarrow \mathrm{H_2} + \mathrm{I} \\ (3) & \mathrm{H} + \mathrm{I_2} & \rightarrow \mathrm{HI} + \mathrm{I} \\ (4) & \mathrm{H} + \mathrm{H} & \rightarrow \mathrm{H_2} \\ (5) & \mathrm{H} + \mathrm{I} & \rightarrow \mathrm{HI} \\ (6) & \mathrm{I} + \mathrm{HI} & \rightarrow \mathrm{I_2} + \mathrm{H} \\ (7) & \mathrm{I} + \mathrm{H_2} & \rightarrow \mathrm{HI} + \mathrm{H} \\ (8) & \mathrm{I} + \mathrm{I} & \rightarrow \mathrm{I_2}. \end{array}$$

A thermal reaction can, however, only occur to an appreciable extent if it is accompanied by a decrease in free energy. The application of this thermodynamic criterion—which, however, only indicates the possibility of reaction, but gives no information as to whether or not reaction *will* occur—to reactions (2)-(8) yields the result that, under the experimental conditions employed by Warburg, reactions (2), (3), (4), (5), and (8) are thermodynamically possible, but that reactions (6) and (7), which are associated with an *increase* in free energy, are not.* Also reactions (3), (4), and (5) may be neglected in comparison with (2) owing to the concentration of HI being much greater than that of I_2 and to the very small concentrations of the atoms. We thus arrive at the conclusion that, following the primary reaction

$$(1)\ HI + h\nu \rightarrow H + I,$$

the secondary reactions

$$(2)\ H + HI \rightarrow H_2 + I$$

and

$$(8)\ I + I \rightarrow I_2$$

occur, the sum of the whole process being represented by

$$2HI + h\nu \rightarrow H_2 + I_2.$$

One quantum thus decomposes two molecules of HI, one molecule being decomposed directly, the other by a secondary process involving a resultant of the primary process. (The scheme for HBr decomposition is similar in all respects.)

The energy necessary to dissociate the halogen acids into their constituent atoms—the primary process here assumed—has been calculated by Warburg, who obtained the values 89,500 cal. per gram-molecule for HBr and 65,000 cal. for HI. Using more modern values for the heats of dissociation of H_2, Br_2, and I_2, these values become 85,000 or 80,000 cal. for HBr and 70,000 or 65,000 cal. for HI, according as to whether the heat of dissociation of H_2 is taken as 100,000 or 90,000 cal. Reference to Table XXXIX. (p. 421) shows that the

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* The application of this criterion to reaction (2) may be cited as an illustration of the method employed. The condition which must be satisfied for this reaction to be possible is

$$\log_{10} \frac{p_H \cdot p_{HI}}{p_I \cdot p_{H_2}} > \log_{10} K',$$

in which K' is the equilibrium constant for the reaction, and according to Nernst is given by

$$\log_{10} K' = -\frac{Q'}{4{\cdot}57\,T} + \Sigma\nu C.$$

Q' is the heat of reaction, and is the difference between the heats of dissociation of hydrogen and of hydrogen iodide. Taking the values used by Warburg, $Q' = -q_{HI} + q_{H_2} = -64570 + 90000 = 25420$. Placing $T = 291$ yields $\frac{Q'}{4{\cdot}57\,T} = 19{\cdot}1$. Using also the values of Warburg for the chemical constants of reactants and resultants, we find

$$\Sigma\nu C = C_H + C_{HI} - C_{H_2} - C_I = -1{\cdot}4 \cdot (C_{HI} = 3{\cdot}4,\ C_{H_2} = 1{\cdot}6, \text{ and } C_I - C_H = 3{\cdot}2).$$

We obtain, therefore, $\log_{10} K' = -19{\cdot}1 - 1{\cdot}4 = -20{\cdot}5$. Since in the reacting system $p_H = p_I$ and the smallest value of p_{HI} employed was 60 mm. while the largest value of p_{H_2} was 760 mm., the smallest value of the ratio $\frac{p_H \cdot p_{HI}}{p_I \cdot p_{H_2}}$ was 0·08. It follows, therefore, with certainty that reaction (2) is thermodynamically possible.

values of $1/p$ for the wave-lengths 209 and 253 $\mu\mu$ are 135,900 and 112,300 cal. respectively, so that the quantum supplied at both wave-lengths is energetically sufficient to effect a primary dissociation. The same is true for HI at the three wave-lengths employed.

An alternative mechanism for the two reactions was preferred by Stern and Volmer (*Z. wiss. Phot.*, **19**, 275, 1920). The primary process they regarded as the activation of the absorbing molecule, and the secondary process as a reaction between this activated and a non-activated molecule of halogen acid. Thus we have

$$\begin{aligned} HX + h\nu &\rightarrow HX^* \\ HX^* + HX &\rightarrow H_2 + X_2. \end{aligned}$$

The secondary process may, however, occur in stages, which may be of the type indicated by Warburg, i.e. involving atoms.

Bodenstein (*Trans. Faraday Soc.*, **21**, 525, 1926) attempted various methods of differentiating between these two mechanisms, but without arriving at any decision. One method was the determination of the rate of photochemical decomposition of HI in the presence of added iodine. If reaction occurs by Warburg's scheme, then reaction (3) $H + I_2 \rightarrow HI + I$ should take place when the iodine concentration becomes commensurable with that of HI, and the net rate of decomposition should therefore be reduced. Such is indeed found, but it is due to a lessening of the light intensity due to absorption by iodine. Indications were obtained that the observed lowering of reaction rate was greater than this " internal filter action " would account for, but the experiments were not conclusive. Another method of deciding between the two alternative mechanisms was sought for in the effect of addition of an inert gas, for example, nitrogen. If the Stern-Volmer mechanism applies, the yield might then be considerably reduced through deactivation by collision of the light-activated HI molecules before they react. As mentioned already, addition of nitrogen is found to have no effect on the velocity. This result, however, does not invalidate this mechanism, since nitrogen molecules may not be able to deactivate molecules of HI on collision.

Recent chemical and—more especially—physical evidence points strongly to the primary process originally proposed by Warburg being the correct one. The evidence is based on the nature of the absorption spectra of HI and HBr in the ultra-violet and has been discussed in Chapter IV. The work of Bonhoeffer and Steiner (*Z. physikal. Chem.*, **122**, 187, 1926) on HI and of Tingey and Gerke (*J. Amer. Chem. Soc.*, **48**, 1838, 1926) on HI and HBr has shown that no trace of a band spectrum is present in the absorption of either gas and that, as far as could be detected by the high dispersions † used, the absorption spectra are continuous. This result must be interpreted in the sense that the primary process is a direct dissociation of the absorbing molecule of halogen acid into atoms.

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† Bonhoeffer and Steiner used a large Rowland grating, the dispersion of which was more than sufficient to render detectable with HI a band structure of the spacing to be anticipated on the molecular theory of band spectra.

Further evidence supporting the hypothesis of primary dissociation of HI and HBr has been obtained by B. Lewis (*J. Physical Chem.*, **32,** 270, 1928) and Bonhoeffer and Farkas (*Z. physikal. Chem.*, **132,** 235, 1928), and the Warburg mechanism for the photo-decomposition of these gases may now be regarded as definitely established. Lewis (cf. also *Proc. Nat. Acad. Sci.*, **13,** 720, 1927) determined by direct measurement the quantum efficiency of the HI reaction at low pressures of the order of 0·1 mm. Under such conditions, if the Stern-Volmer mechanism is applicable to the reaction, a much diminished quantum yield should be found, since the mean time between collisions becomes greater than the mean life of an activated HI molecule (assumed to be 10^{-7} sec.). Actually, quantum yields in the neighbourhood of 2 were still obtained, indicating that the polar molecule of HI dissociates in one elementary act into atoms when it absorbs a quantum of ultra-violet radiation. Lewis used light of wave-length 208 $\mu\mu$ (corresponding to $1/p = 137{,}000$ cal.). He considers that the surplus energy absorbed by the HI (namely the difference between 137,000 cal. and 68,000 cal., the heat of dissociation) is expended partly as energy of excitation of the resulting I atom (21,000 cal.), the remainder as kinetic energy of the H and I atoms.

Bonhoeffer and Farkas carried out experiments of three types to differentiate between the Stern-Volmer and Warburg mechanisms, obtaining in each case results confirmatory of the latter :—

(1) If HI at sufficiently low pressures be illuminated with ultra-violet light and the Stern-Volmer mechanism holds, fluorescence should be observed, since under these conditions the mean time between collisions is greater than the period required for spontaneous emission of the energy of activation. Tests made with streaming HI gas (at pressures between 2 and 0·0075 mm.) exposed to ultra-violet light revealed, however, no detectable fluorescence.

(2) In agreement with Lewis's results, the quantum yield of HI decomposition at low pressures (0·5 to 0·0075 mm.) was found to be of the same order of magnitude as at high pressures.

(3) The view that primary dissociation of HI into atoms occurs was also confirmed by the observation that when HI at low pressures is exposed to ultra-violet light, there occurs a fall of pressure which can only be attributed to the adsorption of free atoms (H and I) on the walls of the containing vessel. Adsorption of free atoms occurs also when HBr or I_2 is illuminated, and experiments with solid HI also indicate that H atoms may be detached from the solid surface.

The Photochemical Formation of Ozone.—A considerable amount of work has been carried out on this reaction and on the reverse process, photochemical deozonisation. It was Nernst (1894) who first drew attention to the possibility of short wave radiation being able to convert oxygen into ozone, and this was soon after confirmed by Lenard (*Ann. Physik*, **1,** 486, 1900) who found the reaction to proceed with light of wave-length 185 $\mu\mu$. The course of the reaction and the photostationary state attained were studied by Regener (*Ann. Physik*, **20,** 1033, 1906). Starting either with pure oxygen or with ozonised oxygen containing 6 per cent. O_3, the same photostationary concentration of 2·2 per cent. O_3 was obtained under the experimental conditions of this work. The kinetics of these reactions is, according to Bodenstein (*Z. physikal. Chem.*, **85,** 335, 1913), reproduced by the equations

$$+\frac{d[O_2]}{dt} = k_2[O_3] - k_1[O_2] \text{ for the deozonisation process,}$$

and $$+\frac{d[O_3]}{dt} = k_1[O_2] - k_2[O_3] \text{ for the formation of ozone.}$$

The heterogeneous ultra-violet light employed is feebly absorbed by oxygen and strongly by ozone. The rate of ozonisation is proportional to the energy absorbed and the reaction is thus unimolecular when the absorption is weak; the reverse reaction is, however, bimolecular for weak absorption (Weigert, *Z. physikal. Chem.*, **80,** 78, 1912), unimolecular when the absorption is strong.

The quantum yield of the ozonisation reaction was determined by Warburg (ref. (4), p. 429). He employed the dynamic method and, in order to obtain high absorption and thus measurable yields with monochromatic illumination, used high pressures of oxygen—up to 300 atmospheres. The results (cf. Table XL.) show that the quantum yield decreases with increasing pressure at both wave-lengths, and that it is considerably smaller with light of wave-length 253 $\mu\mu$ than with 207 $\mu\mu$. The latter result is not due to loss in photochemical yield of ozone at the longer wave-length by the reverse reaction. Though the absorption of ozone is much stronger at 253 $\mu\mu$, which is practically the maximum of the ozone absorption band, only slight decomposition of ozone occurred under the experimental conditions employed, and the figures in the tables have been corrected for this. It will be observed that with $\lambda = 207$ $\mu\mu$ and pressures not higher than 125 atmospheres the quantum efficiency is in the neighbourhood of 3·0, i.e. three oxygen molecules disappear for each quantum absorbed. Warburg accounted for this by assuming as primary process dissociation of oxygen into atoms

$$(a)\ O_2 + h\nu \rightarrow O + O,$$

and as secondary reactions

$$(b)\ O + O_2 \rightarrow O_3$$
$$(c)\ O + O \rightarrow O_2.$$

Assuming further that the last of these reactions is comparatively infrequent, the net effect will be the sum of (a) and twice (b), that is, one quantum would cause the decomposition of *three* oxygen molecules with the formation of two of ozone. It was recognised, however, by

Warburg (1916) that this mechanism could not apply to the photochemical formation of ozone with light of wave-length 253 $\mu\mu$, since the energy supplied is not sufficiently great to effect the postulated primary process. He estimated the heat of dissociation of oxygen to be greater than 136,000 cal., whilst the value of $1/p$ for 253 $\mu\mu$ is but 112,300 cal. The mechanism of the reaction with light of this wave-length must then involve activated oxygen molecules, and Warburg suggested the scheme represented by

$$O_2 + h\nu \rightarrow O_2^* \quad . \quad . \quad . \quad . \quad (1)$$

followed by

$$O_2^* + O_2 \rightarrow O_3 + O \quad . \quad . \quad . \quad (2)$$

or by

$$O_2^* + 2O_2 \rightarrow 2O_3 \quad . \quad . \quad . \quad . \quad (3)$$

In either case, if all the activated molecules succeed in reacting the quantum efficiency would be three.† Owing to the uncertain value of the heat of dissociation of oxygen, Warburg was doubtful whether even with light of wave-length 207 $\mu\mu$ the primary process could be regarded as a dissociation. His view appeared to be that Einstein's Law could only be expected to apply when primary dissociation occurred, and that when wave-lengths were employed such that $1/p < q$ ($q =$ heat of dissociation) reaction would still be possible though characterised by smaller quantum yields.

Recent physical determinations make it very probable that the primary process in this reaction for the wave-lengths under consideration is not dissociation into atoms. Sponer and Birge (cf. p. 207) have found that the convergence limit of the oxygen absorption bands occurs at about 175 $\mu\mu$ and that approximately the same wave-length corresponds to the energy necessary for dissociation (163,000 cal.). It is thus probable that the mechanism of photochemical ozone formation with light of $\lambda = 207$ and 253 $\mu\mu$ is one involving activated oxygen molecules as in the second formulation of Warburg.

A good criterion of the validity of Einstein's Law is that ϕ, the number of moles of photolyte disappearing per calorie of radiation absorbed, should increase with increasing λ. Although this is the case in the photochemical decomposition of HI and HBr and in a few other reactions, the reverse is generally true; ϕ is either constant or decreases as the wave-length is increased, in agreement with usual photochemical experience that radiation of short wave-length is photochemically more effective than radiation of long wave-length. This is the case in the reaction under consideration, the photochemical ozonisation of oxygen. As already stated, however, Warburg accounted for the deficiency in yield with light of wave-length 253 $\mu\mu$ by the assumption of a reaction mechanism different from that with light of wave-length 207 $\mu\mu$. In the former case, quantum absorption was assumed only to result in the formation of activated oxygen molecules, and energy of activation might thus be lost before reaction. But even with $\lambda = 207$ $\mu\mu$ (when primary dissociation was assumed to occur) loss of energy may also take place, as shown by the decrease of quantum yield with increase of pressure. Warburg explained this effect of pressure by the assumption that energy may be dissipated "during the act of absorption." A coupling between the absorbing molecule and its neighbours was postulated, so that the energy absorbed might be shared among the molecules so coupled together, and the greater the pressure of the system the less the likelihood that the energy remaining in the absorbing molecule would be sufficient to decompose it. If, however, we discard entirely the hypothesis of primary dissociation in this reaction, it is not clear how the diminution in quantum yield with increase of pressure is best to be interpreted. In that event, i.e. postulating a reaction mechanism involving activated molecules, collisions between activated and non-activated oxygen molecules become necessary for reaction to occur, and the quantum yield should depend only on the ratio of the probabilities of reaction and of deactivation on collision—a ratio which is independent of the pressure.† It is, however, probable that in such systems under high pressure simple kinetic considerations of the above type are not applicable, and that the effect of pressure on quantum yield is related in some way to the "electromagnetic field" about the absorbing molecule.

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† It appears doubtful whether with light of $\lambda = 253$ $\mu\mu$ the activation of the oxygen is even sufficient to permit of reaction (2). Taking the heat of dissociation of O_2 as 163,000 cal. and the heat evolved on conversion of two moles of ozone into three of oxygen as 68,000 cal., it is found that $2O_2 = O_3 + O - 115{,}500$ cal. This will represent, therefore, the energy of activation of an oxygen molecule necessary to enable (2) to proceed, provided that we assume that the reverse reaction requires no energy of activation. The energy supplied by the light ($\lambda = 253$ $\mu\mu$) is only 112,300 cal.; it is, however, possible that the difference might be made up from the kinetic energy of the colliding molecules.

An alternative—and possibly preferable—formulation of the mechanism of photochemical ozonisation of oxygen under high pressure has been advocated by Wulf (*J. Amer. Chem. Soc.*, **50,** 2596, 1928), who suggested that with light of wave-lengths 207 $\mu\mu$ and (especially) 253 $\mu\mu$ the absorbing entity is not the O_2 molecule, but the polymer O_4. Also, it was considered that for wave-lengths less than 240 $\mu\mu$ primary dissociation of the absorbing O_4 molecule occurs, viz. $O_4 \rightarrow O_3 + O$, while with longer wave radiation formation of activated O_4 molecules ensues. The existence of such a limiting wave-length is, according to Wulf, suggested by the character of the absorption, is not in disagreement with thermal data, and would afford a simple explanation of Warburg's results.

The Decomposition of Ozone.—The photochemical decomposition of ozone in ultra-violet light has been studied by Regener (*Ann. Physik*, **20,** 1033, 1906), von Bahr (*ibid.*, **33,** 589, 1910), and Weigert (*Z. physikal. Chem.*, **80,** 78, 1912). The first-named found that with complete absorption of the radiation the velocity of decomposition is approximately proportional to the concentration of ozone. Von

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† If ternary collisions ($O_2^* + 2O_2$) are necessary for reaction to occur, one might even expect the quantum yield to *increase* with increasing pressure.

Bahr also found a unimolecular course, but in her experiments the ozone concentration was so small that only a small proportion of the light was absorbed. This result is unexpected, since the apparent order of reaction should be the greater the less complete the absorption. The effect of pressure was also investigated by von Bahr and an increase in the reaction velocity observed when the total pressure of the system was diminished to below 200 mm. Hg; at 10 mm., for example, the velocity constant was seventeen times greater than at 200 mm. pressure. Weigert confirmed Regener's result of the unimolecular course of the reaction for complete absorption, and found that with decreasing extent of absorption the apparent order increases, the maximum order determined experimentally being about 1·4 when the absorption was of the order of 50 per cent.

The quantum efficiency of the deozonisation process in ultra-violet light was determined by Warburg (ref. (7), p. 429). The majority of his experiments were carried out with monochromatic light of wave-length 253 $\mu\mu$, which approximates to the maximum of the strong ozone absorption band in the ultra-violet. Mixtures of ozone with oxygen, with nitrogen, and with helium were employed, the total pressure being one atmosphere, and the influence of water vapour on the rate of decomposition was also tested. With dry ozonised oxygen it was found that the quantum sensitivity is dependent on the concentration of ozone. When the ozone content of the mixture is high, γ decreases with decreasing ozone concentration; on the other hand, in weakly ozonised oxygen—containing less than 0·5 volume per cent. of ozone—γ is independent of the ozone content. This is shown in Table XLV., in which $c =$ concentration of ozone (volume per cent.), $E =$ energy absorbed (cal.) per sec., $A =$ fraction of incident radiant energy absorbed, and $\gamma =$ quantum efficiency.

TABLE XLV.

PHOTOCHEMICAL DECOMPOSITION OF OZONE (WARBURG).

Dry Ozonised Oxygen. $\lambda = 253\ \mu\mu$.

High Ozone Concentrations.				Small Ozone Concentrations.			
c.	$E \cdot 10^6$.	A.	γ.	c.	$E \cdot 10^6$.	A.	γ.
9·29	275	1	3·52	0·47	449	0·752	0·29
2·92	200	0·95	1·66	0·47	354	0·752	0·26
1·85	227	0·98	0·76	0·35	328	0·558	0·28
0·75	244	0·94	0·50	0·18	160	0·288	0·31
						Mean	0·285

With mixtures of ozone and nitrogen (containing practically no oxygen) an analogous result was obtained, yet the limiting value of the quantum efficiency for weak ozone concentrations is 3·8 times greater, i.e. 1·09. In explanation of the different limiting values in the presence of nitrogen and of oxygen, Warburg proposed a mechanism in which the primary process is a dissociation of ozone according to

$$O_3 + h\nu \rightarrow O_2 + O \quad . \quad . \quad . \quad . \quad (1)$$

In ozonised oxygen the following secondary processes are then possible :—

$$O + O \rightarrow O_2 \quad . \quad . \quad . \quad . \quad (2)$$
$$O + O_2 \rightarrow O_3 \quad . \quad . \quad . \quad . \quad (3)$$
$$O + O_3 \rightarrow 2O_2 \quad . \quad . \quad . \quad . \quad (4)$$

Of these secondary processes, (2) does not affect the concentration of ozone, (3) increases it, and (4) decreases it. The quantum efficiency of the primary process is unity, that of the total reaction should therefore lie between 0 and 2 depending on the relative extents of the secondary processes. When nitrogen is used as a diluent to the ozone, there is the possibility of disturbing reactions between oxygen atoms or ozone and nitrogen. Tests carried out to detect oxides of nitrogen in such mixtures on insolation with light of wave-length 253 $\mu\mu$ yielded negative results, and it must be concluded that nitrogen acts as a chemically indifferent gas in this reaction. In the N_2—O_3 mixtures employed by Warburg, the only oxygen present was that formed by reactions (1), (2), and (4), and thus reaction (3) would occur to a much smaller extent than in ozonised oxygen. If, as is permissible, we postulate complete non-occurrence of this reaction in mixtures of ozone and nitrogen, the quantum efficiency would be expected to be between 1 and 2. This conclusion is experimentally confirmed ; in dilute ozonised oxygen γ is 0·3, in nitrogen 1·09. When helium was substituted for nitrogen as the diluent gas, however, an unexpected result was obtained. Instead of obtaining the same value of γ as in the presence of nitrogen, the higher value of 1·7 was found. It does not appear that Warburg's theory is able to account for this difference, unless it is assumed that helium and nitrogen exert different catalytic effects on reaction (2) or reaction (4).

Before dealing further with the specific influence of various inert gases on this reaction, Warburg's results for the quantum sensitivity of moist ozonised oxygen of high ozone content will be considered. It has already been noted that in dry ozonised oxygen γ increases with increasing ozone concentration when the latter exceeds 0·5 per cent. The same behaviour is observed when the gas mixtures are saturated at ordinary temperatures with water vapour ; the quantum yields are, however, about twice as great as in dry mixtures of like composition. It is also found that the value of γ for a given moist mixture of ozone and oxygen decreases with increasing incident intensity of illumination, and that the empirical equation $\gamma = B\sqrt{\frac{c}{E}}$ (c = concentration of ozone, E = incident light intensity, B = constant for a given wave-length) reproduces within the experimental error the dependence of γ on these factors. Experiments with light of the three wave-lengths 209, 253, and 287 $\mu\mu$ showed that the value of the constant B is least for light of $\lambda = 253$ $\mu\mu$, i.e. when the absorption is greatest. This result probably implies that the absorption of radiant energy is attended by a deozonising effect which is the greater the greater the volume in which the absorption occurs. In mixtures containing a high concentration of ozone—especially when moist—quite large values of γ may be obtained. The largest value found by Warburg was 8, observed in an experiment with light of wave-length 209 $\mu\mu$ and an ozone concentration of 8 per cent. Such high yields imply a " chain " mechanism for the process (cf. p. 447), the energy of the exothermic reaction $2O_3 \rightarrow 3O_2$ being utilised in producing activation and decomposition of further molecules of ozone. It was suggested by Warburg that this activation may be due to energy-rich oxygen molecules formed by reaction (2) $O + O \rightarrow O_2$. Only with high concentrations of ozone would the probability of collision of such activated molecules with ozone molecules become appreciable.

Ozone is also decomposed by visible light (Griffith and Shutt, *J.C.S.*, **119**, 1948, 1921 ; **123**, 2752, 1923), the most effective wave-lengths being in the red and yellow portions of the spectrum. With constant intensity of illumination, the rate of deozonisation of ozone-oxygen mixtures at atmospheric pressure and containing up to 11 per cent. (by volume) of ozone was found to be nearly proportional to the square of the ozone concentration. Since the absorption of ozone in this region of the spectrum is feeble, this result may be written in the form $\frac{dx}{dt} = kI_{\text{abs.}}[O_3]$, where $I_{\text{abs.}}$ = energy absorbed. Kistiakowsky (*Z. physikal. Chem.*, **117**, 337, 1925) re-investigated this reaction, extending the measurements to mixtures much stronger in ozone (prepared by the method of Riesenfeld and Schwab, *Ber.*, **55**, 2088, 1922), and following the course of the reaction at different pressures. With pressures of ozonised oxygen greater than 100 mm. Hg, he finds the course of reaction to be given by $\frac{dx}{dt} = \frac{k_1 I_{\text{abs.}}[O_3]^{\frac{1}{2}}}{[O_2]}$; on the other hand, at low pressures, below 10 mm., the reaction is no longer retarded by O_2 and the velocity depends only on the rate of energy absorption, i.e. $\frac{dx}{dt} = k_2 I_{\text{abs.}}$. The quantum sensitivity under the latter conditions was found to be 2 molecules of ozone per quantum ; at higher pressures γ obviously depends on the concentrations of both ozone and oxygen. The highest value of γ experimentally realised was 2·8 ; it is clear, however, that with high concentrations of ozone and small concentrations of oxygen much greater values might be obtained.

The influence of foreign gases on the rate of photochemical deozonisation has been studied by von Bahr (*loc. cit.*) and Warburg for the reaction in ultra-violet light ; and by Griffith and MacWillie

(*J.C.S.*, **123,** 2767, 1923) and Kistiakowsky (*loc. cit.*) in visible light. Von Bahr detected no difference in the effects of air, carbon dioxide, and oxygen on the reaction rate; in the other investigations cited, specific effects were found. Griffith and MacWillie compared the reaction velocities in gases of composition x per cent. of ozone, $10x$ per cent. of oxygen with those in mixtures containing x per cent. of ozone, $10x$ per cent. of oxygen, and $(100 - 11x)$ per cent. of diluent gas. The diluents employed were helium, argon, nitrogen, carbon monoxide, and carbon dioxide, and the rate of photochemical deozonisation is in the order given of the gases, that in the presence of helium being the greatest. None of these gases absorbs in the visible, and, with the exception of carbon monoxide, none reacts with ozone photochemically activated. In all cases the reaction velocity is greater than that in ozonised oxygen of the same ozone concentration. These results were interpreted in the sense that the gases employed as diluents exert a smaller retarding effect than does oxygen. Assuming the primary process to be

$$O_3 + h\nu \rightarrow O_3 \text{ (activated)}$$

and that the secondary reaction

$$O_3 \text{ (activated)} + O_3 \rightarrow 3O_2$$

follows, the simplest explanation is that the relative catalytic activities of the various gases on the rate of deozonisation are in inverse ratio to the readiness with which they deactivate an activated ozone molecule on collision. This leads to the view that the probability of an activated ozone molecule retaining its excess energy after collision with another gas molecule is greatest for helium, argon, and nitrogen in the order given, less for carbon monoxide and carbon dioxide, and least of all for oxygen. Kistiakowsky arrived at the same conclusion and expressed the reaction rate in the presence of inert gases by the equation

$$\frac{dx}{dt} = \frac{kI_{\text{abs.}}[O_3]^{\frac{1}{2}}}{[O_2] + a[X]},$$

in which [X] is the concentration of the indifferent gas and a is a constant which has the value 0·13 for helium and 0·28 for nitrogen. Warburg's results for deozonisation in the ultra-violet in the presence of helium, nitrogen, and oxygen have already been mentioned; on the whole it would appear better to interpret them in this same way, rather than by the mechanism involving oxygen atoms which was postulated by Warburg. It is of interest that the thermal decomposition of ozone at 100° C. is also influenced by the addition of chemically indifferent gases. Griffith and McKeown (*J.C.S.* **127,** 2086, 1925; *Trans. Faraday Soc.*, **21,** 597, 1926) find that for mixtures of ozonised oxygen with any one of the gases argon, nitrogen, carbon dioxide, and helium, the velocity of thermal deozonisation is greater than that found for ozonised oxygen containing the same partial pressure of oxygen. The thermal reaction, however, differs from the photochemical in that each of these diluent gases exerts in the former case a specific positive catalytic effect over and above that due to mere displacement of oxygen; that is, the velocity of thermal deozonisation is increased by adding one of these gases to ozonised oxygen at constant volume. Also, the order in which the gases affect the velocity is different in the two cases; while helium has the greatest effect on the photochemical reaction velocity, its influence on the thermal decomposition is less than that of nitrogen, argon, or carbon dioxide. It is thus probable that the mechanism by which the "catalytic" action of these inert gases operates is different in the two modes of decomposition. While in the photochemical decomposition the assumption of different efficacies of the inert gases in deactivating energy-rich ozone molecules will satisfactorily account for the experimental results, the thermal reaction may best be interpreted in terms of a mechanism expressed by the equations

$$O_3 \rightarrow O_3^* \quad . \quad . \quad . \quad . \quad . \quad (a)$$
$$O_3^* + O_3 \rightleftharpoons \text{complex} \quad . \quad . \quad . \quad (b)$$
$$\text{Complex} \rightarrow 3O_2 \quad . \quad . \quad . \quad . \quad (c)$$

Here the complex molecule formed by (*b*) is assumed to be capable of decomposing on collision with any other molecule present, the collision resulting either in the reversal of (*b*) or in reaction (*c*), depending on the nature of the colliding molecule. A collision of the complex with oxygen is assumed to favour the re-formation of ozone, while collision with any of the inert gases is more favourable to reaction (*c*) than to the reversal of (*b*).

Brief mention may also be made of the behaviour of mixtures of ozonised oxygen and hydrogen on exposure to ultra-violet light (Weigert and Böhm, *Z. physikal. Chem.*, **90,** 194, 1915) and to visible light (Griffith and Shutt, *J.C.S.*, **123,** 2752, 1923). In both cases two reactions occur, deozonisation and a reaction between ozone and hydrogen with formation of water, most probably by the process $O_3 + H_2 \rightarrow H_2O + O_2$. The velocity of the deozonisation reaction $2O_3 \rightarrow 3O_2$ is considerably greater than that found in the absence of hydrogen under otherwise identical conditions. Thus, in ultra-violet light addition of small quantities of hydrogen—up to 8 per cent.—produces an increase in the rate of the reaction $2O_3 \rightarrow 3O_2$ proportional to the concentration of hydrogen; further additions are, however, not attended by further increase in the velocity. The maximum rate obtained is about eight times that found in the absence of hydrogen. In visible light, mixtures of the composition x per cent. O_3, $8{\cdot}4x$ per cent. O_2, $(100 - 9{\cdot}4x)$ per cent. H_2 were investigated, and the rates of deozonisation compared with those found in mixtures of composition x per cent. O_3,, $(100 - x)$ per cent. O_2. The ratio of the velocity in the former case to that in the latter increased from 4·1 when $x = 8{\cdot}6$ (per cent. hydrogen = 19) to 9·7 when $x = 3{\cdot}3$ (per cent. hydrogen = 69). Since the effect of hydrogen on this reaction is considerably greater than that of any of the chemically indifferent gases helium, argon, etc., Griffith and Shutt attributed it to a different cause. It was suggested that the water molecules formed by the simultaneous reaction, and which might possess for some period after their formation an appreciable excess energy, are able to activate ozone molecules on collision. The reaction $O_3 + H_2 \rightarrow H_2O + O_2$ is attended by an energy evolution of 92,000 cal. per gram-molecule of water formed. Together with the energy of activation of ozone supplied by the radiation (40,000 cal.), this amounts to 132,000 cal. shared between the resultant water and oxygen molecules.

The Photochemical Decomposition of Nitrous and Nitric Oxides.—Macdonald (*J.C.S.*, p. 1, 1928) has studied these photochemical reactions, employing ultra-violet light of wave-length 1860-1990 Å. Nitrous oxide decomposes according to the equation $4N_2O \rightarrow 2NO + O_2 + 3N_2$, and the proportions of the products remain constant over a considerable variation of the conditions. The quantum efficiency of the reaction (mean $\lambda = 190\ \mu\mu$) was found to be 3·9 molecules of N_2O decomposed per quantum and to be constant between 0° and 40°, though with increase of temperature the rate of decomposition increases markedly (1·47 times per 10° rise) owing to increasing absorption of light by the N_2O. The mechanism suggested by Macdonald for the reaction is that expressed by

$$\begin{aligned} &(a)\ N_2O + h\nu \rightarrow N_2O^* \\ &(b)\ N_2O^* + N_2O \rightarrow O_2 + N_2 + 2N \\ &(c)\ 2(N + N_2O \rightarrow NO + N_2), \end{aligned}$$

but his estimate that reaction (*b*) is energetically possible is almost certainly in error. The energy of a quantum of wave-length 190 $\mu\mu$ is 150,000 cal. per mole, but, taking the value 250,000 cal. for the heat of dissociation of nitrogen, reaction (*b*) requires an energy of activation of 285,000 cal. Even with $D_{N_2} = 125{,}000$ cal. which is clearly too low, reaction (*b*) is hardly possible under the experimental conditions employed. The proposed mechanism cannot therefore be accepted, though, in view of the fact that a chain seems to be excluded by the observed independence of γ on the experimental conditions, it is not easy to suggest an alternative one. Lind (*J. Physical Chem.*, **32**, 573, 1928), who has studied various gas reactions initiated by α-rays (radiochemical reactions), compares the photo-decomposition of N_2O with the radiochemical decomposition (Wourtzel, *Le Radium*, **11**, 342, 1919). Both decompositions are stoichiometrically identical, viz. $4N_2O \rightarrow 3N_2 + 2NO_2$ (or $2NO + O_2$), and the quantum yield ($\gamma = 4$) appears to be the same as the "ion-yield." Lind suggests that both processes have essentially the same mechanism, *clustering* of three N_2O molecules about an ionised N_2O molecule in the one case and about an excited N_2O molecule in the other. The ionised and excited states are presumed to have sufficiently long lives for this "clustering" to occur.

Nitric oxide decomposes photochemically in two ways, stoichiometrically according to

$$(1)\ 2NO \rightarrow N_2 + O_2$$

and

$$(2)\ 3NO \rightarrow N_2O + NO_2.$$

The major reaction is (1), the volume of N_2O formed being only about 10 per cent. of that of oxygen. The quantum yield (molecules of NO decomposed per quantum) is 1·45. The reaction mechanism suggested by Macdonald regards the major process (1) as

$$(\alpha)\ NO^* + NO \rightarrow N_2 + O_2$$

and the subsidiary process (2) as a trimolecular reaction

$$(\beta)\ 2NO + NO^* \rightarrow N_2O + NO_2.$$

Reaction (β) is at least plausible, since at least three thermal gas reactions of NO (with O_2, with Cl_2, and with Br_2) are trimolecular.

Reactions with High Quantum Yields. — Before discussing other cases in which comparatively simple behaviour is found, it is convenient here to introduce an account of the explanations advanced to interpret the very high quantum yields found in certain photochemical reactions, of which the best known is the hydrogen-chlorine reaction. Other examples exhibiting high values of γ are the photochemical chlorinations of CO and CH_4, the decomposition of H_2O_2, and the bromine-sensitised conversion of maleic ester into fumaric ester. Such processes demand for their interpretation some kind of " chain " mechanism. This type of mechanism consists of a cycle of reactions whose resultants are activated molecules, radicals, or atoms, which again enter into reaction initiating a fresh sequence of reactions. A " chain " is thus established, whose length is the number of times the cycle is on the average repeated, and the same number (or some simple multiple of it) gives the quantum efficiency of the process. At least three types of chain mechanism have been proposed in which the carriers of the chains are (*a*) electrons, (*b*) activated molecules, and (*c*) atoms respectively. All three mechanisms were originally applied to the hydrogen-chlorine reaction, the most studied of these reactions. The first explanation—in which free electrons were postulated as catalyst—was advanced by Bodenstein (*Z. physikal. Chem.*, **85,** 329, 1913). It was assumed that the primary process is a photoelectric effect and that subsequently secondary processes take place. The scheme in the case of the H_2—Cl_2 reaction, for example, was essentially

$$Cl_2 + h\nu \rightarrow Cl_2^+ + \ominus \quad . \quad . \quad . \quad (1)$$
$$\ominus + Cl_2 \rightarrow Cl_2^- \quad . \quad . \quad . \quad . \quad (2)$$
$$Cl_2^- + H_2 \rightarrow 2HCl + \ominus \quad . \quad . \quad . \quad (3)$$

The electron resulting from (3) reacts again according to (2), and so on, a large number of HCl molecules thus being formed as a result of absorption of but one quantum of radiation. This hypothesis did not long survive, however, owing to the fact that no ionization is detectable in illuminated chlorine.* The activated molecule theory was later proposed also by Bodenstein (*Z. Elektrochem.*, **22,** 58, 1916). Applied to the combination of hydrogen and chlorine, it may be formulated by the equations

$$\begin{aligned}&Cl_2 + h\nu \rightarrow Cl_2 \text{ (activated)}\\&Cl_2 \text{ (activated)} + H_2 \rightarrow 2HCl \text{ (activated)}\\&HCl \text{ (activated)} + Cl_2 \rightarrow Cl_2 \text{ (activated)} + HCl.\end{aligned}$$

The chain is maintained, according to this scheme, by activated molecules of the resultant HCl, which transfer some of their excess energy to chlorine molecules by collision. This theory will be discussed more fully in Chapter X. in connection with the kinetics of hydrogen-chlorine combination; its weakness when applied to very photosensitive systems is the necessary assumption that the activated molecule can only be deactivated by a given molecular species and that other molecules exert practically no influence on it by collision. Thus in the hydrogen-chlorine reaction, where the chain is of great length, it is necessary to postulate that practically no dissipation of energy occurs when the activated molecule of HCl collides with hydrogen or with other HCl molecules, but that the excess energy is retained until it collides with a chlorine molecule. From this point of view, the assumption of atoms or radicals as the carriers of the chain seems a more probable one than that which postulates molecules in higher quantum states. Such an atom-chain mechanism was first advanced in explanation of the high quantum yield of the hydrogen-chlorine reaction by Nernst (*Z. Elektrochem.*, **24,** 335, 1918). Nernst originally assumed that the primary reaction caused by the absorption of light by the chlorine is dissociation into atoms, i.e. $Cl_2 + h\nu \rightarrow 2Cl$. This formulation of the primary process was later discarded (cf. Warburg, *Z. Elektrochem.*, **27,** 139, 1921) in favour of a mechanism which attributes the formation of chlorine atoms to a secondary process, but as this modification does not affect the type of chain mechanism postulated it will not be discussed further at present. The chain reactions which follow the production of chlorine atoms are, according to Nernst,

$$Cl + H_2 \rightarrow HCl + H \quad . \quad . \quad . \quad (1)$$
$$H + Cl_2 \rightarrow HCl + Cl \quad . \quad . \quad . \quad (2)$$

These processes recur, until the chain is broken by one or other of the reactions

$$H + H \rightarrow H_2 \quad . \quad . \quad . \quad . \quad (3)$$
$$H + Cl \rightarrow HCl \quad . \quad . \quad . \quad . \quad (4)$$
$$Cl + Cl \rightarrow Cl_2 \quad . \quad . \quad . \quad . \quad (5)$$

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* J. J. Thomson, *Proc. Camb. Phil. Soc.*, **11**, 90, 1901; Lenard, *Heidelberger Akad. Ber.*, Nr. **28,** 31, 32, 1910; Ludlam, *Phil. Mag.*, **23**, 757, 1912; Le Blanc and Volmer, *Z. Elektrochem.*, **20**, 494, 1914.

Owing to the very small concentrations of atoms in a reacting system, reactions (3) to (5) occur relatively infrequently, so that a very high quantum yield is possible. On the basis of his " Heat Theorem " and by methods similar to those employed by Warburg for the photochemical decomposition of HI and HBr, Nernst showed that reactions (1) and (2) are thermodynamically possible. In his calculations, however, he employed the old value (106,000 cal.) for the heat of dissociation of chlorine. If we substitute the later and more accurate value of 57,000 cal., it is found that reaction (1), instead of being exothermic to the extent of 25,000 cal. as stated by Nernst, is really accompanied by practically no heat effect. While this to some extent weakens the case for a chain of this type, it does not disprove it; reaction between Cl and H_2 may still occur with sufficient frequency to operate a "chain." Nernst pointed out that the analogous reaction in the case of hydrogen-bromine combination, viz. $H_2 + Br \rightarrow HBr + Br$, is endothermic to the extent of 15,000 cal., and thus cannot take place to an appreciable extent at ordinary temperatures. This is in agreement with the experimental finding of Pusch (*Z. Elektrochem.*, **24,** 336, 1918), that hardly any hydrobromic acid is formed when a mixture of hydrogen and bromine is strongly illuminated. On the other hand, at temperatures above 150° photochemical combination does occur, and this must be attributed to the occurrence of the reaction between Br and H_2, the energy of activation (15,000 cal.) of the reactants being supplied by the kinetic energy of translation of the molecules in the reacting system.

The Nernst mechanism applied to the hydrogen-chlorine reaction ascribes the retarding effect of certain impurities, notably oxygen, to combination of these with hydrogen atoms and chlorine atoms, thus causing a diminished concentration of the latter. Thus, when oxygen is the inhibitor, it forms ClO_2 with the chlorine atoms and is then regenerated by reaction of ClO_2 with atomic chlorine; a small amount of oxygen present may thus greatly diminish the photochemical yield and yet its concentration remain constant. Other chain mechanisms involving atoms have been proposed for the $H_2—Cl_2$ reaction, as also have other theories of the action of inhibitors; these are considered in Chapter X.

An experimental proof that the photochemical union of hydrogen and chlorine is indeed a long " chain " reaction has been obtained by Weigert and Kellermann (*Z. physikal. Chem.*, **107,** 1, 1923). These workers illuminated mixtures of hydrogen and chlorine by means of a spark discharge and determined the time which must elapse before formation of HCl becomes detectable. The extent of reaction was estimated by application of the Töpler " Schliermethode," which depends on a change in the refractive index of the gas, the change in the present instance being due to a change in chemical composition and to the increase in temperature brought about by the positive heat of reaction (Draper Effect). Employing photographic and other means, Weigert and Kellermann found that no effect was observable

1/10,000th second after illumination, and that the maximum effect took place between 1/300th and 1/40th second after illumination. It was further established that the time necessary for the maximum effect to be produced was the greater the more sensitive the gas mixture, i.e. the greater the quantum yield. The experiments thus show that on activating the mixture by illumination of very short duration (spark discharge), a relatively long time of 1/100th second elapses while "dark" chemical reactions proceed, and that the sensitivity of a given mixture of hydrogen and chlorine is a measure of the length of the "chain" of these dark reactions.

Reference may here be made again to the experiments of Porter, Bardwell, and Lind (*J. Amer. Chem. Soc.*, **48**, 2603, 1926), which also lead to the conclusion that the combination of hydrogen and chlorine either on illumination or when subjected to α-rays is a chain reaction. They found that the ratio of the quantum yield to the radiochemical yield † is constant for gas mixtures with very different sensitivities, and that the ratio has the value 1 : 4. Since each α-particle forms a positive and a negative ion, the yield per ion is twice the yield per quantum. This might mean either that the chains in the case of ionisation are twice as long, or that there are twice as many of them. The former assumption is clearly inadmissible in view of the constancy of the ratio of the two yields with different gas mixtures. Lind and his co-workers therefore accept the second view, namely, that whether the chain be initiated by light or by α-particles, it has the same length in the same gas mixture, but that in the latter case twice as many chains are started. Accepting the Nernst mechanism, they suggest the following processes as preliminaries to the chain reaction. In light:

$$\begin{gathered} Cl_2 + h\nu \rightarrow Cl_2^* \\ Cl_2^* + Cl_2 \rightarrow Cl_2 + 2Cl, \end{gathered}$$

the latter reaction having an efficiency of 50 per cent. For α-radiation:

$$\begin{aligned} &Cl_2 + (\alpha) \rightarrow Cl_2^+ + \ominus;\ Cl_2 + \ominus \rightarrow Cl_2^- \\ &Cl_2^+ + H_2 \rightarrow Cl_2H_2^+ \\ &Cl_2^- + H_2 \rightarrow Cl_2H_2^- \\ &Cl_2H_2^+ + Cl_2H_2^- \rightarrow 2H_2Cl_2^* \\ &2H_2Cl_2^* + 2Cl_2 \rightarrow 4HCl + 4Cl, \end{aligned}$$

again arriving at the Nernst chain.

Very interesting results have been obtained by Marshall (*J. Physical Chem.*, **29**, 842, 1453, 1925) in connection with the effect of pressure on the length of the "chain" in the hydrogen-chlorine reaction. In his first paper, experiments are described in which hydrogen atoms prepared by Wood's method (*Proc. Roy. Soc.*, **102**A, 1, 1922) were passed successively into chlorine and bromine, and the yields of HCl and of HBr compared. Assuming that in Br_2 one hydrogen atom forms one molecule of HBr, it is found that in Cl_2 the number of HCl molecules formed per hydrogen atom increases from 1 at a pressure of 0·04 mm. to 7 at 6·0 mm. pressure. In the second paper, it is shown that analogous results are obtained for the *photochemical* union of hydrogen and chlorine. The range of pressures investigated was from 0·01 mm. to 60 mm., and the quantum yield in this range increased from 20 to 25,000. In these experiments the hydrogen was present in considerable excess; the dependence of the quantum yield on the relative pressures of hydrogen and chlorine was not determined. The wave-length of the light employed was 300-400 $\mu\mu$ (mean 350 $\mu\mu$). The amounts of energy absorbed were not directly determined but were calculated from the data of Coblentz, Long, and Kahler (*Bureau of Standards Technical Papers*, No. 330) and of Harrison and Forbes (*J. Optical Soc.*, **10,** 1, 1925) on the energy emitted by quartz mercury lamps and on the spectral distribution of the energy, and the data of von Halban and Siedentopf (*Z. physikal. Chem.*, **103,** 7, 1922) on the extinction of chlorine. While there may be some uncertainty attached to the absolute values of the quantum sensitivity, these experiments should give the correct relative effect of pressure on the quantum yield. Marshall considered that his results are better interpreted in terms of the Bodenstein "hot-molecule" theory than in terms of the Nernst atom-chain theory, and also advances a number of objections to the latter.

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† This term denotes the number of HCl molecules formed by each ion-pair produced in the gas by α-rays.

Chains involving atoms have also been postulated for other reactions of the halogens, both sensitised and non-sensitised reactions. The best known examples are the photochemical union of hydrogen and bromine (Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, **114,** 208, 1924), the reaction between iodine and potassium oxalate (Berthoud and Bellenot, *Helv. Chim. Acta*, **7**, 307, 1924), the bromination of stilbene, cinnamic acid, and the nitrile of α-phenylcinnamic acid (Berthoud, *Trans. Faraday Soc.*, **21,** 560, 1926), and the bromine-sensitised conversion of the ethyl ester of maleic acid into fumaric ester (Eggert and Borinski, *Physikal. Z.*, **25,** 19, 1924; Eggert, *ibid.*, **26,** 865, 1925; Wachholtz, *Z. physikal. Chem.*, **125,** 1, 1927). In the previous Chapter it has already been stated that the velocity of certain of these reactions is proportional to the square root of the light intensity, and it is this that points strongly to the intervention of halogen atoms in these processes. Considering first the photo-reaction between iodine and potassium oxalate in aqueous solution, Berthoud and Bellenot (*loc. cit.*) showed that the reaction velocity is given by the expression

$$+\frac{d[CO_2]}{dt}=\frac{kI_0^{\frac{1}{2}}[I_t]^{\frac{1}{2}}[K_2C_2O_4]}{[KI]} \quad . \quad . \quad . \quad (A)$$

in red light, when the absorption is weak, and by

$$+\frac{d[CO_2]}{dt}=\frac{k'I_0^{\frac{1}{2}}[I_t]^{-\frac{1}{2}}[K_2C_2O_4]}{[KI]} \quad . \quad . \quad (B)$$

in blue light, when the absorption is practically complete. In these equations k and k' are constants, $[I_t]$ is the concentration of titratable iodine, i.e. the sum of the concentrations of I_2 and KI_3, and I_0 is the light intensity. These equations may be deduced on the basis of the reaction mechanism suggested by Berthoud. The primary process is assumed to be dissociation of I_2 (but not of KI_3 or I_3' ions) into atomic iodine—

$$I_2 + h\nu \rightarrow 2I \quad . \quad . \quad . \quad . \quad (1)$$

The primary reaction is then followed by the secondary processes

$$I + I \rightarrow I_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$2I + I' \rightarrow I_3' \quad . \quad . \quad . \quad . \quad . \quad (3)$$
$$C_2O_4'' + I \rightarrow C_2O_4' + I' \quad . \quad . \quad . \quad (4)$$
$$C_2O_4' + I_2 \rightarrow 2CO_2 + I + I' \quad . \quad . \quad . \quad (5)$$

Reactions (4) and (5) constitute chain processes, in which atomic iodine is regenerated, while processes (2) and (3) break the chains. In order to explain the retarding effect of KI on the reaction velocity, it is further necessary to assume that reaction (3) is considerably faster than (2).* Berthoud also considered it necessary to postulate that the rate of disappearance of iodine atoms by (4) is slow compared with that by (2) or by (3). The obvious objection that this would entail a yield much less than that predicted by the Einstein relation was supposed to be obviated by the assumption of the chain reactions (3) and (4). This is not correct, however; if the probability of iodine atoms combining with each other is greater than the probability that they react with oxalate, quantum efficiencies greater than unity are impossible, whereas Berthoud and Bellenot obtained quantum yields of about 25 in blue light. It is, however, possible to deduce the correct kinetic equation for the photo-reaction on the basis of the above mechanism without having to make Berthoud's assumption. We have

$$+\frac{d[CO_2]}{dt} = k_5[C_2O_4'][I_2].$$

Since every (unstable) C_2O_4' ion formed is assumed to react with I_2 according to (5), it follows that the velocity of (5) is equal to that of (4), i.e.

$$+\frac{d[CO_2]}{dt} = k_5[C_2O_4'][I_2] = k_4[C_2O_4''][I] \quad . \quad . \quad (6)$$

The reaction velocity is thus determined by the concentration of oxalate and the stationary-state concentration of iodine atoms. The latter is obtained as follows. When the absorption of light is weak, the velocity of formation of iodine atoms by the primary process is equal to $k_1 I_0[I_2]$; iodine atoms are also formed in reaction (5), so that their rate of formation is

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* This appears to be a weakness in the theory (cf. also p. 491).

$$+\frac{d[I]}{dt} = k_1 I_0[I_2] + k_5[C_2O_4'][I_2] = k_1 I_0[I_2] + k_4[C_2O_4''][I].$$

The rate of disappearance of iodine atoms is, if process (2) be neglected in comparison with (3),

$$-\frac{d[I]}{dt} = k_3[I]^2[I'] + k_4[C_2O_4''][I].$$

Since the unstable intermediate product (iodine atoms) never appears in detectable amounts, its rate of disappearance must equal its rate of formation at all stages of the reaction (except during a brief initial period).* We thus find

$$+\frac{d[I]}{dt} = k_1 I_0[I_2] + k_4[C_2O_4''][I] = -\frac{d[I]}{dt} = k_3[I]^2[I'] + k_4[C_2O_4''][I],$$

from which

$$[I] = \sqrt{\frac{k_1 I_0[I_2]}{k_3[I']}}.$$

Substituting this value of [I] in equation (6), we obtain

$$+\frac{d[CO_2]}{dt} = k_4 \cdot \sqrt{\frac{k_1}{k_3}} \cdot \frac{I_0^{\frac{1}{2}}[I_2]^{\frac{1}{2}}[C_2O_4'']}{[I']^{\frac{1}{2}}}.$$

This equation may be transformed into the kinetic equation (A) obtained experimentally (p. 451) by substituting for $[I_2]$ the value $K \,.\, [I_3']/[I']$ obtained from consideration of the equilibrium $KI + I_2 \rightleftharpoons KI_3$, and by putting $[I_3'] = [I_t]$, an allowable approximation provided that the concentration of KI is not too small. One thus obtains

$$+\frac{d[CO_2]}{dt} = \frac{kI_0^{\frac{1}{2}}[I_t]^{\frac{1}{2}}[C_2O_4'']}{[I']},$$

in which

$$k = \frac{k_4 k_1^{\frac{1}{2}} K^{\frac{1}{2}}}{k_3^{\frac{1}{2}}}.$$

When the absorption is complete, as is the case when blue light is employed, Berthoud and Bellenot (*J. Chim. phys.*, **21**, 336, 1924) show that the same mechanism leads to equation (B) (p. 451), i.e. the velocity is now *inversely* proportional to the square root of the concentration of iodine and, if oxalate is present in excess, thus increases as the reaction progresses. It is to be noted, however, that this reaction course (corresponding to equation (B)) applies only if the insolated solution is not stirred; with strong absorption and very energetic stirring the reaction should be zero-molecular with respect to iodine. Actually, it was found that stirring did produce an effect in the predicted direction, but it was not possible to obtain mixing sufficiently rapid to give a reaction of zero order.

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* This postulation of stationary-state concentrations of unstable intermediate products in photochemical and thermal reactions has been discussed and justified by Bodenstein (*Ann. Physik*, **82**, 836, 1927) and by Christiansen (*Z. physikal. Chem.*, **128**, 430, 1927).

Results of considerable interest and importance for the theory of photo-bromination have been obtained by Berthoud (*Trans. Faraday Soc.*, **21**, 560, 1926)* in an investigation of the rates of photochemical addition of bromine to the unsaturated organic compounds stilbene, cinnamic acid, and the nitrile of α-phenylcinnamic acid. The last of these reactions is reversible, the opposing decomposition of the dibrom-compound being photosensitised by bromine.† Considering the first and second of these reactions and dealing only with the case when the absorption of light energy is feeble, it is found that the velocity of bromination in CCl_4 solution is given by

$$+\frac{d[\mathrm{ABr_2}]}{dt} = kI_0^{\frac{1}{2}}[\mathrm{Br_2}]^{\frac{3}{2}},$$

in which A denotes the acceptor molecule. The rate is again proportional to the square root of the light intensity, but is independent of the concentration of acceptor so long as this is not too small. This result may be interpreted with Berthoud on the basis of the following reaction scheme:—

$$\begin{array}{llr}
\mathrm{Br_2} + h\nu & \rightarrow \mathrm{2Br} & (1) \\
\mathrm{A} + \mathrm{Br} & \rightarrow \mathrm{ABr} & (2) \\
\mathrm{ABr} + \mathrm{Br_2} & \rightarrow \mathrm{ABr_2} + \mathrm{Br} & (3) \\
\mathrm{2ABr} & \rightarrow \mathrm{A_2} + \mathrm{Br_2} \text{ or } \mathrm{2ABr} \rightarrow \mathrm{A_2Br_2} & (4)
\end{array}$$

The quantum yield with both acceptors (cinnamic acid and stilbene) is high; according to Berthoud, about 20 molecules are brominated per quantum absorbed. It will be observed that the mechanism postulated involves a chain, but that the chain is not broken by combination of bromine atoms with each other but by reaction (4), combination of two molecules of the unstable monobromide, the other active agent in the chain. The following equations will then apply:—

$$+\frac{d[\mathrm{Br}]}{dt} = k_1I_0[\mathrm{Br_2}] + k_3[\mathrm{ABr}][\mathrm{Br_2}]\,; \quad -\frac{d[\mathrm{Br}]}{dt} = k_2[\mathrm{A}][\mathrm{Br}]\,;$$

hence $$k_1I_0[\mathrm{Br_2}] + k_3[\mathrm{ABr}][\mathrm{Br_2}] = k_2[\mathrm{A}][\mathrm{Br}] \qquad (5)$$

Also,

$$+\frac{d[\mathrm{ABr}]}{dt} = k_2[\mathrm{A}][\mathrm{Br}]\,; \quad -\frac{d[\mathrm{ABr}]}{dt} = k_3[\mathrm{ABr}][\mathrm{Br_2}] + k_4[\mathrm{ABr}]^2\,;$$

hence $$k_2[\mathrm{A}][\mathrm{Br}] = k_3[\mathrm{ABr}][\mathrm{Br_2}] + k_4[\mathrm{ABr}]^2 \qquad (6)$$

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* Cf. also *J. Chim. phys.*, 24, 213, 1927; *Helv. Chim. Acta*, **10**, 289, 1927.

† Cf. p. 606.

Combining equations (5) and (6),

$$k_4[\mathrm{ABr}]^2 = k_1 I_0[\mathrm{Br}_2]$$

or

$$[\mathrm{ABr}] = \frac{k_1^{\frac{1}{2}}}{k_4^{\frac{1}{2}}} I_0^{\frac{1}{2}}[\mathrm{Br}_2]^{\frac{1}{2}}$$

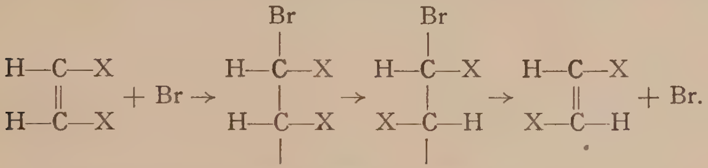
Finally

$$+\frac{d[\mathrm{ABr}_2]}{dt} = k_3[\mathrm{ABr}][\mathrm{Br}_2]$$

$$= \frac{k_3 k_1^{\frac{1}{2}}}{k_4^{\frac{1}{2}}} \,.\, I_0^{\frac{1}{2}}[\mathrm{Br}_2]^{\frac{3}{2}}$$

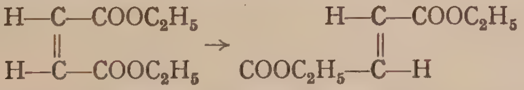
agreeing with experiment.

The above mechanism has an interesting application to the transformation of geometrical isomers (*cis* form ⇌ *trans* form), reactions which are often sensitised by bromine and iodine. Berthoud has suggested that the reaction proceeds via bromine (or iodine) atoms, and that the sensitised transformation *cis* → *trans* may be represented by



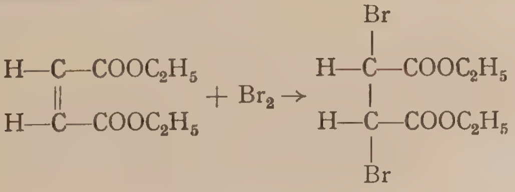
$$\begin{array}{c}\mathrm{H{-}C{-}X}\\ \| \\ \mathrm{H{-}C{-}X}\end{array} + \mathrm{Br} \rightarrow \begin{array}{c}\mathrm{Br}\\ | \\ \mathrm{H{-}C{-}X}\\ | \\ \mathrm{H{-}C{-}X}\\ | \end{array} \rightarrow \begin{array}{c}\mathrm{Br}\\ | \\ \mathrm{H{-}C{-}X}\\ | \\ \mathrm{X{-}C{-}H}\\ | \end{array} \rightarrow \begin{array}{c}\mathrm{H{-}C{-}X}\\ \| \\ \mathrm{X{-}C{-}H}\\ \cdot \end{array} + \mathrm{Br}.$$

In the unstable monobromide formed one of the carbon atoms is trivalent and may thus rotate on the other, with the final production of the *trans*-isomer and a free bromine atom. The results of earlier work do not appear to be inconsistent with this mechanism. In particular, Berthoud cites an investigation of Chavanne and Latiers (*Bull. Soc. chim. Belgique*, **31,** 73, 1913) on the isomerisation of the bi-iodoethylenes $C_2H_2I_2$. Since this date, a very complete study of the velocity of isomerisation of maleic ester in presence of bromine has been carried out by Eggert and his co-workers, who eventually adopt the same mechanism as Berthoud. If the diethyl ester of maleic acid either in the pure liquid state or in CCl_4 solution be exposed to blue or green light in the presence of dissolved bromine, the reaction



$$\begin{array}{c}\mathrm{H{-}C{-}COOC_2H_5}\\ \| \\ \mathrm{H{-}C{-}COOC_2H_5}\end{array} \rightarrow \begin{array}{c}\mathrm{H{-}C{-}COOC_2H_5}\\ \| \\ \mathrm{COOC_2H_5{-}C{-}H}\end{array}$$

takes place. This bromine-sensitised reaction is accompanied, however, by a second reaction occurring to a much smaller extent, namely the photochemical bromination



$$\begin{array}{c}\mathrm{H{-}C{-}COOC_2H_5}\\ \| \\ \mathrm{H{-}C{-}COOC_2H_5}\end{array} + \mathrm{Br}_2 \rightarrow \begin{array}{c}\mathrm{Br}\\ | \\ \mathrm{H{-}C{-}COOC_2H_5}\\ | \\ \mathrm{H{-}C{-}COOC_2H_5}\\ | \\ \mathrm{Br}\end{array}$$

The characteristics of both processes are summarised in the succeeding table. The first column gives the experimental conditions, the second column the quantum efficiency (ϕ) of the transposition reaction, i.e. the number of molecules of maleic ester converted into fumaric ester per quantum absorbed by the bromine, and the third column the quantum efficiency (α) of the bromine-addition reaction.

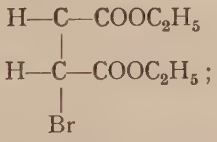
TABLE XLVI.

QUANTUM EFFICIENCIES ϕ AND α IN MIXTURES OF MALEIC ESTER AND BROMINE.

Experimental Conditions.	ϕ. (Transposition.)	α. (Addition.)
21° C.; 436 $\mu\mu$; $0{\cdot}1N$ Br_2	295	8·2
Alteration of intensity of illumination.	ϕ and α independent of intensity between the limits 1·5 and 0·25 HK.	
Alteration of ratio $\frac{\text{ester}}{CCl_4}$.	ϕ and α independent of the ester concentration within the limits of pure ester and 70 moles CCl_4 to 1 mole ester.	
Alteration of reaction temperature.	ϕ and α markedly dependent on temperature. Above 20° the temperature coefficients are greater, below 20° less than those given by $\phi_{23{\cdot}5°} = 2 \times \phi_{19{\cdot}5°}$	$\alpha_{25°} = 2 \times \alpha_{17°}$.
Alteration of concentration of bromine.	ϕ is independent of $[Br_2]$ between the limits $0{\cdot}03N$ and $0{\cdot}3N$.	α is directly proportional to $[Br_2]$ within the same limits.
Alteration of ratio $\frac{\text{maleic ester}}{\text{fumaric ester}}$.	ϕ is dependent on ester ratio.	α is independent of ester ratio.
Alteration of λ of activating light.	ϕ and α are dependent on size of quantum; for blue light ($\lambda = 436$ $\mu\mu$) and green light ($\lambda = 546$ $\mu\mu$) it is found, independently of the temperature, $\frac{\phi_{436}}{\phi_{546}} = 1{\cdot}9$.	$\frac{\alpha_{436}}{\alpha_{546}} = 2{\cdot}0$.

It will be seen from this table that the absorption of one $h\nu$ of 436 $\mu\mu$ by $0{\cdot}1N$ Br_2 in pure maleic ester causes simultaneously 295 molecules to be isomerised and 8 to be brominated. These values of ϕ and α are unaltered by alteration of light intensity and by addition of the chemically indifferent carbon tetrachloride to the system. The most marked difference between the two quantum sensitivities is in respect of alteration of bromine concentration; ϕ is independent of $[Br_2]$, α is directly proportional to $[Br_2]$. A third reaction has also been investigated by Eggert, the photochemical addition of bromine to fumaric ester. The results show a very great similarity between this process and the bromination of maleic ester; in fact, the third column of the preceding table applies equally well to either. Mixtures of maleic ester and fumaric ester thus behave with respect to the addition reaction (α) exactly as the pure substances.

Eggert originally interpreted these results in terms of a mechanism which assumed activated bromine molecules of relatively long life (10^{-5} second) and capable of transferring their excess energy to maleic ester molecules in very small amounts, thus accounting for the very high quantum yield of the transposition reaction. The weaknesses of this theory were recognised at the time and it has recently been abandoned (cf. Wachholtz, *Z. physikal. Chem.*, **125,** 1, 1927) in favour of a theory in which bromine atoms are the active agents. It is found that with the aid of certain special hypotheses the results may be accounted for on this basis, if the removal of bromine atoms occurs, not by recombination to form Br_2 molecules, but by another process which takes place at a greater speed. Attention has already been drawn to the fact that the same assumption is implicit in the reaction mechanism proposed by Berthoud for the photo-bromination of stilbene and cinnamic acid. Briefly, the theory proposed by Wachholtz is as follows. Bromine atoms resulting on illumination form an intermediate product of short life period (a Franck "quasi-molecule") with maleic ester molecules on collision. This intermediate product, whose life is calculated to be of the order of 10^{-10} second, may be transformed in three ways: (*a*) by far the greatest number of these quasi-molecules undergo spontaneous molecular rearrangement with the production of fumaric ester molecules and liberation of bromine atoms; (*b*) a certain fraction, however, must be converted into the stable radical



$$\begin{array}{l} \mathrm{H{-}C{-}COOC_2H_5} \\ \quad\;\; | \\ \mathrm{H{-}C{-}COOC_2H_5}\,; \\ \quad\;\; | \\ \quad\;\; \mathrm{Br} \end{array}$$

and (*c*) if during their life period the quasi-molecules collide with Br_2, they react to form dibromsuccinic ester. These assumptions are in agreement with the independence of the quantum yield ϕ on the ester concentration, on the light intensity, and on the bromine concentration, and also with the direct proportionality found between α and the bromine concentration. The difference between the quantum yields in blue light and in green light is attributed to the greater probability that with the larger quantum in the former case bromine molecules should be dissociated into atoms. The addition of Br_2 to fumaric ester is explained on the same theory; here again the bromine atom forms an intermediate product, which on collision with Br_2 reacts to form dibromsuccinic ester. If this collision does not occur, the quasi-molecule decomposes into its constituents.

The reaction scheme for maleic ester and bromine may thus be represented by the equations:

$$\mathrm{Br_2} + h\nu \rightarrow 2\mathrm{Br} \tag{a}$$
$$\mathrm{Br} + \mathrm{Br} \rightarrow \mathrm{Br_2} \tag{b}$$
$$\mathrm{Br} + \mathrm{M} \rightarrow \mathrm{M} \ldots \mathrm{Br} \tag{c}$$
$$\mathrm{M} \ldots \mathrm{Br} \rightarrow \mathrm{F} + \mathrm{Br} \tag{d}$$
$$\mathrm{M} \ldots \mathrm{Br} \rightarrow \mathrm{MBr} \tag{e}$$
$$\mathrm{M} \ldots \mathrm{Br} + \mathrm{Br_2} \rightarrow \mathrm{MBr_2} + \mathrm{Br} \tag{f}$$
$$\mathrm{MBr} + \mathrm{MBr} \rightarrow \mathrm{MBr_2} + \mathrm{M} \text{ or } 2\mathrm{M} + \mathrm{Br_2} \tag{g}$$
$$\mathrm{MBr} + \mathrm{Br} \rightarrow \mathrm{MBr_2} \text{ or } \mathrm{M} + \mathrm{Br_2} \tag{h}$$
$$\mathrm{MBr} + \mathrm{Br_2} \rightarrow \mathrm{MBr_2} + \mathrm{Br} \tag{i}$$

The quasi-molecule is represented by M . . . Br, the stable radical by MBr; M represents maleic ester, and F fumaric ester. The quantum efficiencies of the two reactions are prevented from being infinite by reaction (*e*), the formation of the radical, and by the disappearance of the radical by reactions (*g*) and (*h*). Reasons are given to show that reaction (*i*) can only occur to a small extent, and as previously stated reaction (*c*) must be rapid compared with (*b*). Calculation yields the result that the experimental data are satisfactorily reproduced if it is assumed that one collision in 6000 between bromine atoms and ester molecules leads to the formation of the intermediate product and one in a million to the formation of the radical MBr. The average life of the latter works out to about 10^{-1} sec.

If the results for the photo-bromination of maleic (or fumaric) ester be compared with Berthoud's results for the photochemical addition of bromine to cinnamic acid or stilbene, it is seen that they chiefly differ in respect of the influence of the light intensity. The velocity of the maleic ester reaction is proportional to the light intensity, that of the reactions of the phenyl derivatives to the square root of the light intensity. This difference is attributed to different methods of formation of the dibrom-compound in the two cases; in the reactions of stilbene and cinnamic acid the significant reaction is $\mathrm{ABr} + \mathrm{Br_2} \rightarrow \mathrm{ABr_2} + \mathrm{Br}$, whereas for maleic ester this reaction does not occur to an appreciable extent, but bromination is attributed to a reaction between bromine and a very unstable intermediate product.

The results above given relate to the ethyl ester; Eggert and his co-workers (*Z. Elektrochem.*, **33,** 542, 1927) have also extended the measurements to the methyl ester (in CCl_4 solution) and to the free acid (in aqueous solution). The bromine-sensitised reactions of these substances are very similar to those of the ethyl ester, the chief differences being:

(1) The somewhat greater quantum yields of the reactions of the methyl ester and free acid. For the methyl ester under standard conditions, $\phi = 430$ and $\alpha = 11$; for the free acid $\phi = 430$.

(2) The quantum yields of the reactions of the methyl ester and of the free acid are independent of concentration of ester (or acid) and of light intensity only when the concentration is high; at smaller concentrations, ϕ and α decrease with decreasing concentration and with increasing light intensity.

(3) The dependence of ϕ and α on the wave-length differs from that in the case of the ethyl ester, slightly for the methyl ester reaction, more markedly in the case of the free acid. In the last-mentioned the relation $\phi_{365\mu\mu} : \phi_{436\mu\mu} : \phi_{547\mu\mu} = 5 : 4 : 1$ was obtained.

Result (2) is not unexpected. It can be interpreted in terms of the reaction mechanism given above, since at low concentrations of ester (or acid), bromine atoms disappear by reactions (*b*) and (*h*), instead of by formation of the quasi-molecule M . . . Br (reaction (*c*)). The quantum yields ϕ and α thus tend to fall at low concentrations. The effect of strong light intensities may similarly be explained.

Another reaction associated with a high quantum yield is the photochemical decomposition by ultra-violet light of hydrogen peroxide in aqueous solution. The reaction was studied by Tian (*Compt. rend.*, **151,** 1040, 1910), who found it to follow a unimolecular course. Henri and Wurmser (*Compt. rend.*, **156,** 1012, 1913; **157,** 126, 284, 1913) have determined the quantum efficiency of the process. They also found a unimolecular course, the reaction velocity being proportional to the absorbed energy. In the experiments described in their first paper they employed heterogeneous radiation comprised within the limits 214-298 $\mu\mu$ and obtained a quantum efficiency of about 130. Later, however, they carried out experiments with monochromatic radiation of wave-lengths 280, 256, 230, and 217 $\mu\mu$ and found a value of γ in each case about 5. It would appear that the intensities of illumination in the latter series were much greater than those previously employed, and it may be that this variable has an influence on the quantum efficiency (see p. 410). On the other hand, Kornfeld (*Z. wiss. Phot.*, **21,** 66, 1921) suggests that the different quantum yields in the two sets of experiments might be due to traces of impurity, to which the reaction is markedly sensitive. The latter investigator found, in agreement with Henri and Wurmser and with Mathews and Curtis (*J. Physical Chem.*, **18,** 166, 521, 1914), that the reaction velocity is sensitive to addition of acid and of alkali. The former diminishes the rate of decomposition; small additions (up to 10^{-4} *N*) of alkali have a positive catalytic effect, but further additions are accompanied by a marked retardation of reaction velocity. The quantum efficiency of the reaction was also carefully determined by Kornfeld, the wave-length of the activating light being 315 $\mu\mu$. Values of γ between

7 and 80 were obtained, depending on the concentration of H_2O_2 and the acidity of the solution. γ increases with increasing H_2O_2 concentration, the rate of increase being greatest at low concentrations. Addition of acid diminishes the quantum yield and also diminishes somewhat its dependence on the concentration of H_2O_2. In addition to acid and alkali, however, the reaction is also sensitive to the presence of other substances, some of which promote the decomposition though most act as inhibitors. This sensitivity to traces of foreign material is another characteristic of reactions with high quantum yields, the same phenomenon being met with in the hydrogen-chlorine reaction, the formation of phosgene, and the chlorination of toluene, all of which are inhibited by traces of oxygen. Evidently a chain mechanism must be ascribed to the photochemical decomposition of H_2O_2 and the action of inhibitors attributed—at least in part—to their reducing the length of the chain by reaction with activated molecules or atoms. Kornfeld (*loc. cit.*) has proposed such a reaction scheme for the decomposition of H_2O_2, and, though it is perhaps rather more hypothetical than the majority of attempts to explain photochemical reactions, it presents certain features of interest. It suggests as the process which follows the absorption of light the decomposition of the H_2O_2 molecule with formation of an activated oxygen atom as one of the products. It is further assumed that these activated oxygen atoms may react with H_2O_2 in two ways, according to the extent of activation. One of these reactions is the start of a " chain," the other not. The former will be initiated only by those atoms having a sufficiently large amount of excess energy and will thus be favoured by increasing the frequency of the activating light. Actually, Henri and Wurmser found a slight increase in γ on raising the frequency. While naturally no great stress need be given to the mechanism suggested by Kornfeld, it appears not at all unlikely that considerations of an analogous type might well apply to this and to other reactions in which the quantum yield is high and also diminishes with increasing wave-length.

Preliminary work by F. O. Rice (*J. Amer. Chem. Soc.*, **48,** 2099, 1926) directs attention in quite a different direction. He finds that the *thermal* decomposition of H_2O_2—a reaction which previous work had shown to be very sensitive to inhibitors, surface of containing vessel, presence of colloidal organic matter, etc.—occurs mainly on the surface of small dust particles. By removing the latter, he has been able to prepare an aqueous solution containing 50 per cent. H_2O_2 which has a half-life period at 60° C. of several months. Experiments on the *photochemical* decomposition of H_2O_2 indicate that here again the presence of dust particles is an important factor. Two solutions of H_2O_2 of the same concentration, one of them dust-free, the other not, were illuminated in quartz flasks placed at equal distances from a mercury vapour lamp. The rate of evolution of oxygen in the latter solution was found to be much greater than that in the solution from which dust-motes had been removed. The rate of decomposition of hydrogen peroxide in ultra-violet light in solutions of different dust contents was found to be approximately proportional to the " concentration " of dust, as measured by the light-scattering power of the solution. The true value of the quantum efficiency of the reaction may thus be considerably lower than those found by Kornfeld and Henri and Wurmser; though as yet no direct determinations have been made, Rice suggests that in the absence of dust it is unity. In explanation of these results, which Rice considers likely to be applicable to other photochemical changes with high quantum yields, it is postulated that the substrate is adsorbed on the particles of dust in aggregates, the average number of molecules in which determines the quantum yield. A quantum of light absorbed by a molecule in an aggregate causes the decomposition of all the molecules in the cluster. Thus Marshall's result of increasing quantum yield with increasing pressure in the photochemical union of hydrogen and chlorine is attributed to increasing magnitude of the cluster adsorbed on to dust particles. While these preliminary experiments of Rice are undoubtedly of significance and further work on these lines will be awaited with interest, his view that the phenomenon is of wide application should at present be regarded with reserve.

In addition to the above-mentioned characteristics of reactions with high quantum yield—namely, sensitivity to traces of impurity and dependence of γ on concentration of reactants—it should be noted that they are all exothermic processes. While the energy liberated in such processes as the combination of hydrogen and chlorine and the decomposition of ozone is large, other reactions such as the transformation of maleic ester into fumaric ester are associated with comparatively small heat evolutions. The liberated energy of reaction together with the energy of activation is shared between the products of reaction, and *may* be utilised for activating fresh molecules with ensuing reaction. Theoretically a high quantum yield is possible in all cases in which the reaction is sufficiently exothermic. Thus for the process $A + B + h\nu \rightarrow C + D + Q$ cal., the resultants C and D possess at the instant of their formation the excess energy of Q cal. plus the energy of activation $Nh\nu$. Calling the latter Q_0 and assuming that the excess energy is shared equally between C and D, each gram-molecule of these substances possesses an excess energy of $(Q + Q_0)/2$ cal. If Q is sufficiently great, these molecules are in a position to activate fresh reactant molecules.

We have seen that according to the theory of reaction chains this transfer of energy is effected by collision, or that, alternatively, atoms or radicals are formed which by collision with molecules act as carriers of the chains. Other views regarding the mechanism of the utilisation of the liberated energy of reaction have, however, been advanced. Winther (*Z. physikal. Chem.*, **108,** 236, 1924) suggests that in the photosensitised oxidation of hydriodic acid in aqueous solution—another reaction with a high quantum yield—the transfer of energy from excited I_3' ions to I' ions is effected by radiation. In fact, he has based a general theory of photosensitisation on such a method of energy transfer; the activated molecule of the photosensitiser, e.g. chlorine or an I_3' ion, is supposed to absorb ultra-violet or visible radiation and transform it up to short wave radiation which it emits and which is then absorbed by the reacting species. There does not appear to be any experimental evidence in support of this theory and the author himself regards it only as a tentative working hypothesis. An experiment devised to test for the emission of radiation in a photochemical reaction with a high quantum efficiency was carried out by Kornfeld (*Z. physikal. Chem.*, **108,** 118, 1924) with negative results. The photochemical reaction between CO and Cl_2 is accompanied, when oxygen is present, by a sensitised combination of the latter with CO to form CO_2. This sensitised reaction takes place only in the presence of $COCl_2$. Kornfeld showed that in a quartz vessel containing CO, O_2, and some $COCl_2$, no reaction occurred when the vessel was surrounded by another in which the photochemical combination of CO and Cl_2 was taking place. This result shows that a fluorescence by chlorine in the sense suggested by Winther's theory is not the direct cause of the sensitised reaction.

Baly and Barker (*J.C.S.*, **119,** 653, 1921) have attempted to explain the abnormally high yield in the photochemical combination of hydrogen and chlorine by the assumption of radiation from molecules of HCl to both hydrogen and chlorine molecules. The excess energy in the resultant HCl molecules is assumed to be emitted as infra-red quanta which are absorbed by reactants (either H_2 or Cl_2) initiating fresh combination. Kornfeld and Müller (*Z. physikal. Chem.*, **117**, 242, 1925), Taylor (*Treatise on Physical Chemistry*, p. 1228), and Bowen (*J.C.S.*, **123,** 2328, 1923) have criticised this theory. The latter found that the photochemical dissociation of chlorine monoxide is not associated with a high quantum yield, though it is attended with a considerable evolution of heat. Had Baly's views been of general application, it might have been anticipated that the radiation emitted by Cl_2 or O_2 molecules would have been absorbed by Cl_2O with consequent high quantum efficiency for the total reaction. Taylor (*loc. cit.*) points out that the assumption of transfer of energy (by radiation) to both hydrogen and chlorine is not in agreement with the experiments of Bodenstein and Dux (*Z. physikal. Chem.*, **85,** 297, 1913) and others on the kinetics of the hydrogen-chlorine reaction. Over a certain range of concentration, the velocity is practically independent of the hydrogen concentration and proportional to the square of the concentration of chlorine. Weigert (*Z. physikal. Chem.*, **106,** 428, 1923), however, considers that in the photochemical formation of hydrochloric acid, an emission of radiation is not an unlikely accompaniment of such processes as $H + Cl \rightarrow HCl$, $H + H \rightarrow H_2$, and $Cl + Cl \rightarrow Cl_2$, which possibly intervene in the reaction, and that fresh elementary processes may ensue when chlorine molecules absorb such radiation.

The Photochemical Combination of Hydrogen and Bromine.

—One of the most interesting cases of a close relation between the kinetics of photochemical and thermal processes is that found in the union of hydrogen and bromine. The thorough study of these reactions carried out mainly by Bodenstein and his co-workers has led to results of particular significance, especially in regard to the velocity of reactions involving atoms. Certain of the features which characterise the photochemical reaction have already been mentioned (see pp. 385, 403). We may recall the fact that mixtures of hydrogen and bromine are only feebly photosensitive at ordinary temperatures (Pusch, *Z. Elektrochem.*, **24,** 336, 1918; Kastle and Beatty, *Amer. Chem. J.*, **20,** 159, 1898), but that on increasing the temperature to 200° or 250° marked formation of HBr occurs on illumination (Kastle and Beatty, *loc. cit.;* Lind, *J. Physical. Chem.*, **27,** 55, 1924). The latter result was also confirmed by Anderson,* who found that at 300° the thermal rate of combination is increased when the mixture of the two gases is exposed to the light of a quartz mercury lamp. Also, the photochemical reaction is one of those whose velocity is proportional not to the rate of absorption of energy but to the square root of this quantity, which shows that secondary processes play a determinative part.

The *thermal* reaction between H_2 and Br_2 was investigated by Bodenstein and Lind (*Z. physikal. Chem.*, **57,** 168, 1906) at temperatures between 200° and 300° C. It was found that the velocity is given by

$$+\frac{d[2HBr]}{dt}=\frac{k[H_2]\sqrt{[Br_2]}}{m+\dfrac{[2HBr]}{[Br_2]}},$$

in which m is a constant practically independent of the temperature. The explanation of this reaction course was given much later and independently by Christiansen (*Dansk. Vid. Math. Phys. Medd.*, **1,** 14, 1919), Herzfeld (*Z. Elektrochem.*, **25,** 301, 1919), and Polanyi (*ibid.*, **26,** 50, 1920). According to them, the reaction occurs in the following stages:—

$$Br_2 \rightarrow 2Br \quad . \quad . \quad . \quad . \quad (1)$$
$$Br + H_2 \rightarrow HBr + H \quad . \quad . \quad . \quad (2)$$
$$H + Br_2 \rightarrow HBr + Br \quad . \quad . \quad . \quad (3)$$
$$H + HBr \rightarrow H_2 + Br \quad . \quad . \quad . \quad (4)$$
$$Br + Br \rightarrow Br_2 \quad . \quad . \quad . \quad . \quad (6)\dagger$$

Combination of these by the well-known method of setting up the kinetic equations and eliminating the concentrations of the intermediate products H and Br leads to equation (7) for the velocity of the total reaction—

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* Quoted in Taylor's *Treatise on Physical Chemistry*, p. 1245.

† We retain the same numbering of the equations as employed by Bodenstein.

$$+\frac{d[\mathrm{HBr}]}{dt}=\frac{2k_2[\mathrm{H_2}]\sqrt{\frac{k_1}{k_6}[\mathrm{Br_2}]}}{1+\frac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \quad . \quad . \quad . \quad (7)$$

In this equation k_1, k_2, etc. are the velocity constants of the individual reactions. It will be observed that equation (7) agrees with the empiric equation of Bodenstein and Lind, and that the retardation of the reaction by HBr is ascribed to reaction (4), which removes the hydrogen atoms. The rate of reaction is essentially governed by the rate of process (2), i.e. the rate of reaction of hydrogen molecules with bromine atoms, which are in equilibrium with molecular bromine. Herzfeld (*loc. cit.*) showed that from Lind's measurements of the temperature coefficient of the total reaction together with a knowledge of the equilibrium between molecular bromine and bromine atoms, it is possible to calculate the temperature coefficient of k_2. In this way it is found that only the fraction $e^{-17640/RT}$ of all collisions between H_2 and Br leads to reaction. At 300°, for example, the small fraction 10^{-13} of such collisions is effective, a figure of the same order of magnitude as those obtained in reactions between molecules. The reaction is, of course, strongly endothermic.

The *photochemical reaction* between hydrogen and bromine has been studied by Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, **114**, 208, 1925) who employed temperatures between 160° and 218°. White light of strong intensity was used, the energy absorbed by the bromine was determined bolometrically, and the extent of reaction was measured by spectrophotometric estimation of the residual bromine. The reaction velocity under their experimental conditions is considerably greater (about 300 times) than that at corresponding temperatures in the dark, which increase the mechanism adopted attributes to the increased stationary concentration of bromine atoms in the light. The photochemical reaction rate is given by an equation fully analogous to equation (7) for the dark reaction, and may be written

$$+\frac{d[\mathrm{HBr}]}{dt}=\frac{2k_2[\mathrm{H_2}]\sqrt{\frac{\text{Number of Quanta absorbed}}{\text{Time}\,.\,k_6}}}{1+\frac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \quad . \quad (8)$$

This may be derived from the same mechanism as used for the thermal reaction with equation (1) replaced by

$$\mathrm{Br_2}+h\nu\rightarrow 2\mathrm{Br} \quad . \quad . \quad . \quad . \quad (1a)$$

The temperature coefficient of the reaction (between 160° and 218°) was found to be 1·5, and this figure may, as shown by Bodenstein and

Lütkemeyer, be predicted from the temperature coefficient of the dark reaction (2·0), or from the temperature coefficient of k_2. The results of this investigation must be regarded as strongly supporting the view that bromine atoms intervene in the reaction; otherwise it appears impossible to explain (*a*) the dependence of the rate on the square root of the absorbed energy, and (*b*) the retardation by HBr. The quantum efficiency of the reaction is but of limited interest in view of the marked influence of temperature, light intensity, and concentrations of hydrogen and hydrobromic acid on the yield. Rideal and Lewis (*J. Amer. Chem. Soc.*, **48,** 2553, 1926) carried out calculations upon the data of Bodenstein and Lütkemeyer in order to determine whether the sequence of reactions (2) and (3) could occur several times and thus a chain mechanism be present. They find that in the majority of Bodenstein and Lütkemeyer's experiments the quantum yield lies well below 2, but at the highest temperature employed (218°) and with high concentrations of hydrogen the quantum efficiencies begin to exceed 2 at the start of the reaction, when the concentration of HBr is small.

One of the most interesting results of the comparison of the photochemical reaction with the thermal process is that it makes possible a determination of the constant k_6, the velocity constant of the union of bromine atoms. If it be assumed in the photochemical reaction that each quantum absorbed forms two bromine atoms, division of equation (8) by equation (7) gives

$$+\left(\frac{d[\mathrm{HBr}]}{dt}\right)_{light} : +\left(\frac{d[\mathrm{HBr}]}{dt}\right)_{dark} = \sqrt{\frac{\dfrac{\text{Number of Quanta absorbed}}{\text{Time} \,.\, k_6}}{\dfrac{k_1[\mathrm{Br}_2]}{k_6}}}.$$

The ratio k_1/k_6 is the thermal equilibrium constant of the dissociation of bromine into atoms and is known from the data of Bodenstein and Cramer (*Z. Elektrochem.*, **22,** 327, 1916); also, the number of quanta absorbed per unit time and the concentration of Br_2 are known, and thus the value of k_6 is determined. The interesting result is obtained that only 1 collision in 800 between bromine atoms leads to formation of bromine molecules, and that this figure is independent of the temperature (between 218° and 160°) and of the total pressure between the limits investigated. This result is unexpected. For reactions involving atoms, three factors must be taken into consideration in dealing with the question of reaction or non-reaction on collision. These are (1) the heat effect accompanying the reaction, (2) the steric factor, and (3) whether one or more than one molecule is formed as a result of the reaction. Our knowledge of the steric factor is practically nil, but for exothermic reactions in which an atom is involved and in which there are two or more resultants, the general conclusion is that, apart from the influence of (2), every collision should be effective (Herzfeld, *Ann. Physik*, **59,** 635, 1919). In the case of the reaction

$Br + Br \rightarrow Br_2$, however, in which only one molecule is formed, the system after collision of the two Br atoms contains the whole of the energy liberated by the reaction; in order that a normal Br_2 molecule should result, a collision with a surface or with another molecule is necessary, otherwise the two Br atoms will separate. According to our present views of the life of such a "quasi-molecule," a gas pressure of about 1 mm. suffices to yield sufficient collisions to enable the rearrangement of energy to occur, and one would thus expect—apart from the steric factor—that only at pressures below this would failure to react be detected. Bodenstein and Lütkemeyer's result that only about 0·1 per cent. of the total collisions are effective thus remains unexplained. Recently Bodenstein (*Sitzungsber. Preuss. Akad. Berlin*, p. 104, 1926) has extended these measurements into regions of lower pressure, and has shown that the value of k_6 remains unaltered down to pressures of 100 mm. Below this, at 43 mm. pressure, a decrease in k_6 was found. This observation also remains unaccounted for; theoretically the decrease would be expected at considerably lower pressures.

Further conclusions with respect to the velocities of the individual reactions which appear in the scheme suggested for the formation of HBr may also be drawn (Bodenstein and Jung, *Z. physikal. Chem.*, **121,** 127, 1926). In the denominators of the right-hand terms of the kinetic equations (7) and (8), the term $k_4[HBr]/k_3[Br_2]$ appears. The ratio k_4/k_3 was found in the older measurements of Bodenstein and Lind on the thermal reaction to be of the order 1/10, and appeared to be independent of temperature; the data of Bodenstein and Lütkemeyer for the photochemical reaction are also satisfied by the same value for this ratio. Since, however, in both investigations the term $k_4[HBr]/k_3[Br_2]$ appears only as a comparatively small correction as long as [HBr] is not large, the two sets of experiments could be satisfactorily reproduced by other values of the ratio k_4/k_3 which do not deviate too far from 1/10. Further, in these two investigations it was not proved that k_4/k_3 was really independent of the temperature. To test these points Bodenstein and Jung carried out experiments in the presence of excess of HBr at room temperature in strong sunlight, and at 302° in the dark. They found that $\frac{k_4}{k_3} = \frac{1}{8{\cdot}4}$ and confirmed its independence of the temperature over this wide range. The latter result means either that the heats of activation of both the reactions (3) and (4) are nil or that they are finite and exactly equal. The former hypothesis would appear to be much the more plausible; one thus concludes that only a steric factor is concerned *in the fraction of effective collisions* and that this factor is independent of temperature. Comparing the two exothermic reactions

$$H + Br_2 \rightarrow HBr + Br \quad . \quad . \quad . \quad (3)$$

and

$$H + HBr \rightarrow H_2 + Br, \quad . \quad . \quad . \quad (4)$$

it is seen that the steric factor is more likely to militate against reaction in (4), since presumably collision of the hydrogen atom on the hydrogen side of the HBr molecule is necessary for reaction. The value 1/8·4 for the ratio k_4/k_3 is thus in agreement with these views. One other conclusion—not without interest from a photochemical standpoint—may also be obtained from the above result. If the energy of activation of reaction (4) is nil, then the energy of activation of the reverse process (2) becomes equal to the heat of reaction. We thus obtain

$$Br + H_2 = HBr + H - 17640 \text{ cal.}$$

Combination of this equation with the equations

$$Br_2 = 2Br - 47540 \text{ cal.}$$

and $$2HBr = H_2 + Br_2 - 24180 \text{ cal.}$$

leads to $$H_2 = 2H - 107000 \text{ cal.}$$

Correcting to 0° Abs. gives 106,000 ± 3000 cal. for the heat of dissociation of hydrogen, a value considerably higher than that previously indicated by the work of Langmuir (*J. Amer. Chem. Soc.*, **37**, 417, 1915) and Isnardi (*Z. Elektrochem.*, **21**, 405, 1915). A confirmation of this value by independent methods would appear to be desirable before full reliance can be placed on it, yet, though the method of calculation is roundabout, the basis of the derivation appears to be sound.

In addition to determining the photochemical reaction velocity in mixtures of H_2, Br_2, and HBr, Bodenstein and Lütkemeyer (*loc. cit.*) carried out a few experiments in which added oxygen or water was also present. In neither case was any influence on the rate of combination observed. The former result is of particular importance, since, in the corresponding photochemical union of hydrogen and chlorine, oxygen exerts a strong retarding influence.

The photochemical formation of HI from its elements has not been studied from the kinetic standpoint in so thorough a manner as the corresponding reactions for HCl and HBr. Coehn and Stuckardt (*Z. physikal. Chem.*, **91**, 722, 1916) have found that no HI is formed at 270° on illumination of mixtures of H_2 and I_2 in glass or uviol glass vessels, but that under the influence of shorter wave radiation transmitted by quartz, reaction occurs. Bowen (*J.C.S.*, **125**, 1233, 1924) also found no combination of the two gases at ordinary temperatures in glass vessels. At high temperatures, however, it might be expected that combination could occur in visible light. This might take place by the reactions

$$(a)\ I_2 + h\nu \rightarrow 2I$$
$$(b)\ I + H_2 \rightarrow HI + H, \text{ etc.,}$$

or by

$$(a)\ I_2 + h\nu \rightarrow 2I$$
$$(c)\ I + I_2 \rightleftharpoons I_3$$
$$(d)\ I_3 + H_2 \rightarrow 2HI + I.$$

Reaction (*b*) is much more endothermic than the corresponding reaction in the case of H_2—Br_2 mixtures; reaction (*d*) is also probably endothermic, but both might perhaps be expected to occur sufficiently rapidly on increasing the temperature. Lewis and Rideal (*J. Amer. Chem. Soc.*, **48,** 2553, 1926) claim that photo-combination of H_2 and I_2 may be detected at high temperatures, a reaction they attribute to the intermediacy of iodine atoms. At temperatures of 430° and 466°, a shift from the thermal equilibrium point of the reaction $2HI \rightleftharpoons H_2 + I_2$ in the direction of increasing concentrations of HI was observed when the gas mixtures were exposed to radiation of wave-length longer than 460 $\mu\mu$.

Quantum Yields and Kinetics of other Reactions in Gaseous Systems.—We may now discuss briefly the remaining reactions of Table XL., with the exception of the reactions sensitised by halogens or by mercury vapour and also the photo-combination of Cl_2 with hydrogen and carbon monoxide, which will be reserved for later Chapters. The first of such reactions in the table is *the decomposition of ammonia* in ultra-violet light, studied by Warburg (*Sitzungsber. Preuss. Akad. Berlin*, p. 746, 1911) and by Kuhn (*J. Chim. phys.*, **23,** 521, 1926). The former employed light of wave-length 209 $\mu\mu$ and at room temperatures obtained a quantum efficiency of 0·23. The total pressure of the system was 800-900 mm. and the quantum yield remained the same in pure ammonia and in mixtures of nitrogen and hydrogen (1 : 3) containing but 5 per cent. NH_3. In a later paper (*Sitzungsber. Preuss. Akad. Berlin*, p. 872, 1914) Warburg pointed out that the primary process in this reaction cannot be dissociation into $N + 3H$, since the energy supplied by light of wave-length 209 $\mu\mu$ is not sufficient to effect this. He suggested, as an alternative, the mechanism represented by

$$NH_3 + h\nu \rightarrow NH_3^*$$
$$NH_3^* + NH_3 \rightarrow N_2 + 3H_2,$$

and further that the deficiency in quantum yield is due to non-reactive collisions of the type

$$NH_3^* + NH_3 \rightarrow 2NH_3 + \text{Heat}$$

(deactivation by collision). Collisions which result in chemical reaction might be expected when special portions of the colliding molecules are favourably oriented ; otherwise the excess energy of the excited molecule is dissipated as heat.

Kuhn (*loc. cit.*) employed radiation comprised within the limits of wave-length 202·5 $\mu\mu$ and 214·0 $\mu\mu$, and found that at temperatures between 10° and 20° C., 2 to 2·5 quanta were absorbed for each ammonia molecule decomposed. Further, this quantum yield was independent of the pressure between 900 mm. and 5 mm., and the reaction proceeded smoothly to completion at a speed proportional to the rate of absorption of energy. The most interesting result obtained, however, was that on improving the monochromatism of the light the quantum efficiency of the reaction decreased. Thus, using "monochromatic" light of wave-length 206·3 $\mu\mu$ the ratio $\frac{\text{quanta}}{\text{molecules}}$ increased to 8 or 9. It is to be observed that the light used originally by Kuhn is as monochromatic as that used in most photochemical investigations, and the change in quantum yield on selecting a single wave-length of this light is a somewhat surprising result. Kuhn explains his results by supposing that for reaction to occur absorption by the same molecule of two quanta of slightly different frequencies is necessary. This explanation seems hardly feasible, however; a double activation must be very infrequent owing to the small concentration of once-activated molecules together with the fact that the radiation they must absorb to become doubly activated is also absorbed by normal ammonia molecules. In addition, the hypothesis predicts an influence of concentration on quantum yield, a result not confirmed by experiment. Taylor and Bates (*J. Amer. Chem. Soc.*, **49,** 2438, 1927) have suggested an alternative explanation of Kuhn's result (cf. p. 597), but the question cannot yet be regarded as settled.

Kuhn also investigated (*Compt. rend.*, **178,** 708, 1924) the effect of temperature on the quantum yield of the photo-decomposition of ammonia. With light of wave-length 202·5—214·0 $\mu\mu$, the velocity of photolysis was found to increase by about 50 per cent. for a rise in temperature of 100°, a constant temperature coefficient of 1·05 being obtained over the whole range studied (20° to 500° C.). Thus at 20°, 2·5 quanta must be absorbed to decompose one NH_3 molecule; at 500°, only 0·3 quanta. The course of the reaction at high temperatures is different from that at ordinary temperatures, since in the former case the decrease in velocity as the reaction progresses is much more rapid than is accounted for by the diminished absorption of radiant energy. This effect is due to an inhibition of the reaction—at high temperatures only—by hydrogen; nitrogen has no effect on the velocity. Kuhn interpreted his results in terms of the following mechanism. A molecule of NH_3 absorbs a quantum of average wave-length 206 $\mu\mu$ (corresponding to 128,000 cal. per mole) and is converted into an activated molecule NH_3^*. A fraction of such molecules reverts to the normal state, the remainder react according to

$$(\alpha)\ NH_3^* + NH_3 \rightarrow N_2 + 3H_2 + 106{,}000 \text{ cal.}$$

or to

$$(\beta)\ NH_3^* \rightarrow N + H + H_2 + 5{,}000 \text{ cal.}$$

Atomic nitrogen and atomic hydrogen may then enter into further reactions, especially at high temperatures, and the processes

$$(\gamma)\ N + NH_3 \rightarrow N_2 + H_2 + H + 17{,}000 \text{ cal.}$$

and

$$(\delta)\ H + NH_3 \rightarrow N + 2H_2 - 39{,}000 \text{ cal.}$$

may occur. The assumption of these secondary reactions occurring to an appreciable extent at high temperatures explains how the absorption of a single quantum may cause the decomposition of two or three ammonia molecules. The inhibiting action of hydrogen is attributed to reaction between H_2 and NH_3^*, dissociation of hydrogen being postulated, i.e.

$$NH_3^* + H_2 \rightarrow NH_3 + 2H + 44{,}000 \text{ cal.}$$

(a reaction analogous to the Franck-Cario reaction between H_2 and Hg^*).

In criticism of this reaction scheme, it is to be noted that the value assumed by Kuhn for the heat of dissociation of N_2—140,000 cal.—is certainly too small, and the same is true for his value of 84,000 cal. for the heat of dissociation of H_2. If we substitute the more modern values of 263,000 cal. for N_2 (Sponer, *Z. Physik*, **34,** 622, 1925) and 100,000 cal. for H_2, reaction (β) is at once eliminated since it is attended by an absorption of 64,500 cal. We must therefore rule out the possibility of the appearance of nitrogen atoms in the reacting system, even at 500° C. The intervention of hydrogen atoms is, however, not improbable, as they *may* still be formed either as a result of the reaction

$$NH_3^* + NH_3 \rightarrow N_2 + 2H_2 + 2H + 6000 \text{ cal.},$$

or by collision of hydrogen molecules with activated NH_3 molecules. Reaction (δ) is also much more endothermic than is stated by Kuhn and must also be ruled out.† It would thus seem that if we retain the hypothesis that ammonia decomposition is due essentially to the reaction $NH_3^* + NH_3 \rightarrow N_2 + 3H_2$, the effect of increase of temperature on the quantum efficiency must be due to an increase in the number of collisions favourable to reaction. Admitting further that inhibition by hydrogen is ascribable to the reaction $NH_3^* + H_2 \rightarrow NH_3 + 2H$, one might presume that the probability of energy transfer from activated ammonia molecules to hydrogen molecules becomes the greater, the greater the average kinetic energy of the colliding particles.

Yet, as pointed out in Chapter IV. (p. 241), the work of Bonhoeffer and Farkas (*Z. physikal. Chem.*, **134,** 337, 1928) throws doubt on the hypothesis that activated ammonia molecules are the reacting entities in this photo-reaction. The experimental findings that ammonia at low pressures is decomposed photochemically and exhibits no fluorescence, together with the type of "predissociation" band absorption of ammonia in the ultra-violet, point strongly to the primary process being the formation of an excited molecule, but one which has an exceedingly small life and which decomposes spontaneously before it can collide or fluoresce. Bonhoeffer and Farkas suggest that the products of decomposition are $NH_2 + H$ (or $NH + H_2$), and that the small quantum yields of the photo-reaction are attributable to recombination reactions such as $NH_2 + H \rightarrow NH_3$ and $NH_2 + H_2 \rightarrow NH_3 + H$. The second of these is slightly endothermic and thus would be favoured by increase of temperature, which might explain the observed inhibitory effect of hydrogen when the temperature is raised. Another mechanism, also postulating decomposition of NH_3 into $NH_2 + H$, has been advanced by Taylor and Bates (see p. 597).

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† Direct tests by Bonhoeffer and Boehm (*Z. physikal. Chem.*, **119,** 385, 1926) failed to indicate any trace of reaction between active hydrogen and ammonia.

Finally, mention should be made that measurements of quantum yield in ammonia decomposition have been carried out by Kassel and W. A. Noyes, Jr. (*J. Amer. Chem. Soc.*, **49,** 2495, 1927), who employed short wave ultra-violet light of the range 160-190 $\mu\mu$ and estimated the absorbed radiant energy by an indirect method. The result obtained was that 1·4 quanta are absorbed per molecule of ammonia decomposed; the quantum efficiency in this spectral region would thus appear to be higher than that obtained with $\lambda = 209\ \mu\mu$.†

The decomposition of chlorine monoxide has been studied by Bowen (*J.C.S.*, **123,** 1199, 2328) and by Bodenstein and Kistiakowski (*Z. physikal. Chem.*, **116,** 370, 1925), and exhibits comparatively simple behaviour. In the gaseous state two molecules of Cl_2O are decomposed per quantum of blue light absorbed. The quantum yield is independent of whether the light is absorbed by the chlorine monoxide or by chlorine mixed with it; the latter thus sensitises the photochemical decomposition with the same efficiency as characterises the direct reaction itself. Bodenstein and Kistiakowski showed that small quantities of ClO_2 are formed in the course of the reaction, and Bowen also detected the presence of oxides other than Cl_2O in his experiments. The reaction mechanism according to the latter investigator may be represented either by

$$\begin{array}{lll} (a) & Cl_2O + h\nu & \rightarrow Cl_2O^* \\ & Cl_2O^* + Cl_2O & \rightarrow 2Cl_2 + O_2 \end{array}$$

or by

$$\begin{array}{lll} (b) & Cl_2O + h\nu & \rightarrow Cl_2 + O \\ & Cl_2O + O & \rightarrow Cl_2 + O_2. \end{array}$$

Bodenstein and Kistiakowski substitute for Bowen's second mechanism the following scheme, which indicates how higher oxides of chlorine may be formed :—

$$\begin{array}{lll} Cl_2O + h\nu & \rightarrow Cl_2O^* & \\ Cl_2O^* + Cl_2O & \rightarrow ClO_2 + Cl_3 & \text{or } ClO_2 + Cl + Cl_2 \\ ClO_2 + Cl_3 & \rightarrow 2Cl_2 + O_2 & \text{or } ClO_2 + Cl \rightarrow Cl_2 + O_2 \\ Cl_3 + Cl_3 & \rightarrow 3Cl_2 & \text{or } Cl + Cl \rightarrow Cl_2. \end{array}$$

The mechanism of photosensitisation by Cl_2 is discussed later (cf. Chapter XI.); except for this and for the the relatively high temperature coefficient of 1·09 found by Bodenstein and Kistiakowski, the above reaction schemes satisfactorily represent the experimental data for this reaction. The same process has also been investigated in CCl_4 solution by Bowen. The quantum efficiency is now found to be less than in the gaseous state, about 0·9 molecules per quantum being decomposed. It is uncertain to what this difference is attributable. If the primary process be assumed, as in Bowen's formulation (*b*), to be direct dissociation of the absorbing Cl_2O molecule into Cl_2 and O, it implies different secondary processes in the two cases; on the other hand, taking the primary process as molecular excitation, one might assume that in solution more non-reactive collisions occur, with consequent smaller quantum yield.

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† If this result is substantiated, it might suggest that the mechanism of ammonia decomposition is one involving activated NH_3 molecules; at least, it would be interpreted more readily in terms of an activated molecule theory than by the dissociation theory.

Little can be said about the *photochemical decomposition of nitrosyl chloride*, also investigated by Bowen (*J.C.S.*, **127,** 1026, 1925). With light of wave-lengths between 500 and 438 $\mu\mu$, the quantum yield obtained was 0·5. The initial pressure of the gas was 450 mm., and the reaction was followed to 10 per cent. decomposition only, to avoid the influence of the rapid thermal reverse reaction. It is considered probable by the author that the photochemical reaction involves a direct primary dissociation $NOCl + h\nu \rightarrow NO + Cl$, and that the low quantum yield is due to spontaneous reactions re-forming nitrosyl chloride, possibly *via* the transitory compound $NOCl_2$.

We have seen that in the photochemical formation of hydrochloric acid and in the action of light on mixtures of hydrogen and bromine we have two examples in which the yield of product is very far from that demanded by Einstein's Law. In the former case the yield is excessively large, in the latter the yield of HBr very small at ordinary temperatures. The discrepancies are due to the measured secondary reaction not being equivalent to the primary process, or, in the terminology employed, hydrogen is not a suitable acceptor for the halogens activated by light. That acceptors may be found which react in amount equivalent to the number of quanta absorbed by the halogen was shown by Nernst with Pusch (*Z. Elektrochem.*, **24,** 336, 1918) and Noddack (*ibid.*, **27,** 359, 1921). A suitable acceptor for bromine was found in hexahydrobenzene, after the trial of other hydrocarbons such as hexane and heptane which react to a greater extent than predicted by Einstein's Law. In the case of gaseous mixtures of hexahydrobenzene with bromine, the results obtained, after correcting for a slight thermal reaction between the two gases, were in agreement with the calculated within the experimental error, i.e. for each quantum absorbed one molecule of bromine disappears. Indications were also obtained that benzene vapour might act as a suitable acceptor for bromine; toluene on the other hand reacts at a greater rate than would be anticipated from the rate of activation, and the reaction is followed by an after-effect, a result also found by Andrich and Le Blanc (*Z. wiss. Phot.*, **15,** 148, 183, 197, 1915).

A suitable acceptor for activated chlorine was found by Noddack (*loc. cit.*) in trichlorbrommethane CCl_3Br, a colourless liquid which dissolves chlorine readily. It is unattacked by chlorine in the dark;

on illumination of the mixture by violet light † which is absorbed by the chlorine only, the reaction

$$Cl_2 + 2CCl_3Br \rightarrow 2CCl_4 + Br_2$$

occurs. The process may easily be followed by spectrophotometric estimation of the bromine formed. The reaction was studied by Noddack using light of two wave-lengths, 410 $\mu\mu$ and 449 $\mu\mu$, and it was found that for each quantum absorbed one molecule of chlorine disappears with the production of one molecule of bromine. This reaction afforded the first verification of Einstein's Law in liquid media. Noddack also observed that if carbon tetrachloride was added to the system, the quantum efficiency of the reaction progressively diminished, but this was later shown by Grüss (*Z. Elektrochem.*, **29,** 144, 1923) to be due to traces of impurity in the carbon tetrachloride. The latter investigator found that if the solvent be sufficiently purified, the velocity of the photochemical reaction is independent of the relative concentrations of CCl_3Br and CCl_4, at least until the ratio $\frac{\text{moles } CCl_4}{\text{moles } CCl_3Br}$ exceeds 80. An analogous result was obtained using silicon tetrachloride as a solvent. The reaction is thus a simple one, the yield being that predicted by Einstein's Law, and remaining constant on diluting the reaction mixture with an indifferent solvent. For reaction mechanism, we have again to choose between the one in which activated molecules react with the acceptor,

$$\begin{aligned} &Cl_2 + h\nu \rightarrow Cl_2^* \\ &Cl_2^* + 2CCl_3Br \rightarrow 2CCl_4 + Br_2, \end{aligned}$$

and one in which chlorine atoms function,

$$\begin{aligned} &Cl_2 &&+ h\nu \rightarrow Cl_2^* \rightarrow 2Cl \text{ (or } Cl_2 + h\nu \rightarrow 2Cl) \\ &CCl_3Br &&+ Cl \rightarrow CCl_4 + Br \\ &Br &&+ Br \rightarrow Br_2. \end{aligned}$$

If the former of these mechanisms be the correct one, we have a case in which the activated molecule reacts simply with the acceptor molecule without further simultaneous or side reactions. It must be assumed, however, that deactivation of chlorine molecules does not occur or that only a small fraction of their excess energy is dissipated on collision with solvent molecules. If future work should show that this assumption cannot be justified, then recourse must be made to the second mechanism, in which all chlorine molecules which absorb decompose either spontaneously or on collision with other molecules into atoms.

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† CCl_3Br has an absorption band in the ultra-violet beginning at 335 $\mu\mu$. On illumination with light of this and shorter wave-lengths, it decomposes according to the equation $2CCl_3Br \rightarrow C_2Cl_6 + Br_2$.

CHAPTER IX.

EINSTEIN'S LAW AND PHOTOCHEMICAL REACTION MECHANISM II.

PHOTOCHEMICAL REACTIONS IN LIQUID MEDIA.

Investigations of quantum yield in reactions occurring in liquid solution have practically been confined to cases in which the solvent is either water or carbon tetrachloride. The latter has proved to be a very satisfactory solvent for use when the highly reactive halogens chlorine and bromine appear either as reactants or as resultants. Although Plotnikow (*Z. wiss. Phot.*, **12,** 22, 1919) claims that solutions of chlorine in carbon tetrachloride undergo chemical change on illumination, Grüss (*Z. Elektrochem.*, **29**, 144, 1923) and Benrath and Hertel (*Z. wiss. Phot.*, **23,** 30, 1924) appear to have definitely proved that the carefully purified solvent is stable under such conditions. We have already dealt in the preceding Chapter with certain photochemical reactions in which CCl_4 was employed as a solvent, namely, the maleic ester—fumaric ester reactions (Eggert and Borinski), the chlorination of trichlorbrommethane (Pusch, Noddack), and the decomposition of Cl_2O (Bowen, *J.C.S.*, **123,** 1199, 1923). The latter investigator has also determined the quantum efficiencies of the photolysis of ClO_2 and of NCl_3 in carbon tetrachloride solution. The former reaction is quite analogous to the decomposition of the lower oxide Cl_2O ; in both cases a simple behaviour is observed, the decomposition being 80 to 90 per cent. of the theoretical. The photochemical decomposition of nitrogen trichloride is probably more complex; here the results indicate that more than one molecule of photolyte is decomposed per quantum, although the deviation from unity is not very large. It might perhaps have been expected that a substance as sensitive to mechanical stimulus as nitrogen trichloride would also prove to be very photosensitive, but this appears not to be the case. On the other hand, an etherial solution of NCl_3 is stated to explode on short intensive illumination with light of wave-length 365 $\mu\mu$, and the same applies to the solid explosive substance carbazide CON_6 (Noddack, *Handbuch der Physik*, Vol. XXIII., Chapter 6).

Reactions in Aqueous Solution.—Turning to the discussion of quantum yields of photochemical reactions in aqueous solution, it is found that such processes present in general more complications than do gaseous reactions. Many of them are associated with lower quantum yields than unity; in not a few the value of γ diminishes with increasing wave-length of the activating light, and in the majority the quantum yield varies with the concentration of the photolyte. It is thus clear that in many of these reactions all the absorbing molecules do not succeed in reacting and that processes of deactivation are operative.

Warburg (*Sitzungsber. Preuss. Akad. Berlin*, p. 1228, 1918) has studied the energetics of the photochemical conversion of potassium nitrate into potassium nitrite and oxygen. This reaction is not a simple one, since small additions of acid or of alkali affect the yield. In order to obtain the best yields, the solutions must be slightly alkaline; in Warburg's experiments a concentration of $N/3000$ with respect to alkali was employed. The nitrates of Li, Na, K, Mg, Ca, Sr, and Ba give the same results provided solutions of the same equivalent concentration are employed, but HNO_3 is much less sensitive to light. The following table shows that the quantum efficiency at constant concentration decreases with increasing λ, and with constant wave-length diminishes as the concentration is decreased:—

TABLE XLVII.

PHOTOLYSIS OF AQUEOUS SOLUTIONS OF KNO_3 (WARBURG).

$\lambda(\mu\mu)$.	c.	γ.
207	$N/3$	0·25
207	$N/30$	0·19
207	$N/300$	0·11
253	$N/3$	0·17
282	$N/3$	0·024

If, with Warburg, we assume as primary process the dissociation of the NO_3 group into $NO_2 + O$, we find from thermochemical data and the assumption that the heat of dissociation of oxygen is 163,000 cal., that the energy necessary for the initial photolysis is 103,500 cal. per gram-molecule. The energy supplied at the three wave-lengths employed amounts to 137,000, 112,300, and 100,600 cal. respectively. The condition that the quantum is sufficiently large is thus satisfied at 207 $\mu\mu$ and 253 $\mu\mu$. Yet even with light of 207 $\mu\mu$ Einstein's Law is not obeyed, the photochemical effect being only about a quarter of the calculated value. Warburg contrasts the yield in this case with the nearly theoretical yield obtained with light of this wave-length in photochemical ozonisation, a reaction for which the energy necessary for primary dissociation is greater than that required to decompose the nitrate group or ion. He did not abandon the hypothesis of a primary dissociation when the absorbed quantum is sufficiently great, but ascribed the low quantum yields in this case to loss of energy by "damping" during absorption. In a gas at not too high pressure, it may be assumed that most of the quantum absorbed is available to decompose the absorbing molecule. For a molecule in an aqueous solution, however, it is possible that a considerable fraction of the absorbed energy is shared with solvent molecules before the photochemical reaction sets in. The influence of neighbouring molecules on absorption is shown by the wide absorption bands usually found for solutions, which indicates that a greater "damping" effect is present than in the absorption of gases. According to this view, the larger the quantum absorbed the more likely is primary dissociation to occur. Warburg also concluded from the fact that γ increases with increasing concentration of photolyte that the reaction probably occurs on collision of the absorbing molecule with another non-activated molecule. His views appear in this case to be practically indistinguishable from the assumption of the formation of activated molecules as primary process, followed either by deactivation on collision with solvent molecules or by reaction with non-activated molecules of the same kind.

Warburg's work has recently been criticised by Anderson (*J. Amer. Chem. Soc.*, **46,** 797, 1924), who regards the calculation of quantum relationships in this reaction as unjustified, since the process is one in which a photostationary state is reached and the reverse reaction may not be neglected. According to Anderson, KNO_2 inhibits the reaction, and a "steady" state is soon established when only a small fraction of the KNO_3 originally present has been decomposed. Warburg (*Z. Physik*, **29,** 34, 41, 1924), however, maintains that in his experiments the amount of products formed was too small to influence the correctness of his figures for the quantum yield of the direct photolysis. Anderson's work has been criticised and the essential correctness of Warburg's results upheld by Villars (*J. Amer. Chem. Soc.*, **49,** 326, 1927), who finds no evidence of a photostationary state in this reaction. The opposite conclusion arrived at by Anderson is apparently due to a faulty analytical method for the determination of nitrite. Villars found that the quantum efficiencies for wavelengths longer than 280 $\mu\mu$ were very small, and also that with light of wave-length 254 $\mu\mu$ and with $1N$ solution of KNO_3 the quantum efficiency increased with increasing p_H, reaching a value of 0·25 at $p_H = 9{\cdot}9$ and then remaining constant as the p_H was further increased.

Another reaction investigated by Warburg is the reciprocal transformation of maleic and fumaric acids in aqueous solution (*Sitzungsber. Preuss. Akad. Berlin*, p. 960, 1919). The acid stable at ordinary temperatures is fumaric acid; if a solution of either of these acids is subjected to ultra-violet radiation, a stationary state is eventually reached in which the ratio of concentration of maleic acid to that of fumaric acid is in the neighbourhood of 7 to 3. In contrast to the *bromine-sensitised* conversion of the ethyl ester of maleic acid to fumaric ester in CCl_4 solution, which is attended with a very high quantum yield, the direct isomerisation of maleic acid in aqueous solution as well as the reverse process is but feebly photosensitive. Table

XLVIII. summarises the experimental results, which have been corrected in each case for the opposing reaction.

TABLE XLVIII.

$\lambda(\mu\mu)$.	Maleic Acid → Fumaric Acid.		Fumaric Acid → Maleic Acid.	
	γ		γ	
	$c = 0{\cdot}0102$.	$c = 0{\cdot}00514$.	$c = 0{\cdot}0102$.	$c = 0{\cdot}00306$.
207	0·032	0·037	0·104	0·08
253	0·043	0·049	0·098	0·087
282	0·032	0·035	0·133	0·10

The yields in the isomerisation of maleic acid are only about 1/25th of the calculated, those of the reverse reaction about 1/10th. The influence of wave-length is small and irregular; that of concentration also is not great, yet curiously it acts in opposite directions in the two cases. Warburg interprets the low yields in both reactions through the assumption that the primary process is a driving apart of two portions of the absorbing molecules, but that after this separation reunion of the parts may occur either to form the original molecule or to form the isomer. The extent to which the latter occurs is governed only by considerations of probability and is small in both reactions.

Complicated behaviour is also found in the photolysis of the chlorplatinic acids in aqueous solution studied by Boll (*Compt. rend.*, **157,** 115, 1913; *Ann. Chim. Phys.*, **2,** 1, 1914). These endothermic reactions which result in the reduction of the photolyte are apparently bimolecular, and the value of γ increases with increasing concentration of absorbing substance at constant wave-length and diminishes with increasing wave-length at constant concentration. The effect of variation of λ on the quantum yield of the photolysis of the tetra-acid $PtCl_4(OH)_2H_2$ is shown in Table XLI. (p. 425); the effect of concentration (with light of $\lambda = 253\ \mu\mu$) by the following figures:—

PHOTOLYSIS OF $PtCl_4(OH)_2H_2$.

$\lambda = 253\ \mu\mu$

$c \,.\, 10^4$ . . .	0·2	0·5	1·0	2·0
γ . . .	0·26	0·93	1·9	3·5

Results of a similar type were obtained by Vranek (*Z. Elektrochem.*, **23,** 336, 1917) in a study of the photochemical decomposition of potassium cobaltioxalate in aqueous solution. The reaction proceeds according to the equation

$$2K_3Co(C_2O_4)_3 \rightarrow 2CoC_2O_4 + 3K_2C_2O_4 + 2CO_2.$$

Solutions of the cobaltioxalate possess two absorption bands with heads at $\lambda = 426\ \mu\mu$ and $\lambda = 605\ \mu\mu$ respectively, but only wave-lengths within the former band are effective in promoting decomposition. The apparent order of the reaction is between one and two, yet Vranek states that the value of γ (for a given wave-length) is independent of the concentration. This must be regarded as doubtful, however, in view of what is found for other reactions in aqueous solutions which have been investigated. The results given in Table XLI. (p. 425) show that the quantum efficiency falls with increasing λ, but not so markedly as in the photolysis of chlorplatinic acid. It is of interest to note the large difference between the temperature coefficients of the thermal and photochemical reactions in this case. The thermal decomposition of $K_3Co(C_2O_4)_3$ (in aqueous solution) which has a unimolecular course has the high temperature coefficient of 4·56 (between 60° and 70°), while that of the photochemical reaction is only 1·06.

The last reaction to be considered and for which the dependence of γ on wave-length and concentration has been thoroughly studied is the photolysis of HI in hexane and in water (Warburg and Rump, *Z. Physik*, **47**, 305, 1928). It will be recalled that the photochemical decomposition of HI both in the pure liquid and in the gaseous state forms a beautiful illustration of the exact applicability of Einstein's Law; in hexane solution and especially in aqueous solution, however, the reaction is more complex. The results obtained by Warburg and Rump for the photolysis in hexane solutions are summarised in Table XLIX., in which the concentration of HI is expressed in moles per litre.

TABLE XLIX.

PHOTOLYSIS OF HI IN HEXANE (WARBURG AND RUMP).

$\lambda(\mu\mu)$.	[HI].	γ.
207	0·08	1·01
222	0·01	1·20
222	0·08	1·23
222	0·36	1·35
222	0·54	1·41
222	0·80	1·52
222	1·05	1·50
282	0·08	1·58
282	0·28	1·69
282	0·80	1·78
282	0·89	1·82
282	1·16	2·10

The table shows that the quantum yields obtained are between 1 and 2, that they increase with increasing concentration of photolyte, and that (somewhat unexpectedly) they increase with increasing wave-length. The effect of concentration may simply be accounted for if one assumes that after the primary process $HI + h\nu \rightarrow H + I$, the fraction of the resulting H atoms which react according to $H + HI \rightarrow H_2 + I$ increases as the concentration of HI is increased. The diminution of γ with decrease in λ may possibly be due to the fact that the absorption coefficient increases on passing from $\gamma = 282\ \mu\mu$ to $\gamma = 222\ \mu\mu$, hence that in the latter case the concentration of the hydrogen atoms during the photolysis is greater than in the former, and thus there is the greater probability of the occurrence of reactions $H + H \rightarrow H_2$ or $H + I \rightarrow HI$, with consequent falling off in the quantum yield.

The photolysis in aqueous solution was investigated with light of four wave-lengths 207, 222, 253, and 282 $\mu\mu$. With light of $\lambda=282\ \mu\mu$, correction was necessary and was applied for the fact that the absorption of an aqueous solution containing both HI and I_2 is considerably (four or five times) greater than the sum of the separate absorptions of solutions of HI and I_2. This excess absorption, which is due to formation of HI_3, is also present with light of wave-length 253 $\mu\mu$, but in this case its amount could not be estimated, so that we give values of γ only for the three wave-lengths 207 $\mu\mu$, 222 $\mu\mu$, and 282 $\mu\mu$.

TABLE L.

PHOTOLYSIS OF HI IN AQUEOUS SOLUTION (WARBURG AND RUMP).

[HI].	γ		
	207 $\mu\mu$.	222 $\mu\mu$.	282 $\mu\mu$.
0·8	0·336	0·078	0·114
3·75	0·959	0·455	0·457
7·5	2·21	1·21	0·538

Except for the increase in γ at the smaller concentrations in passing from 222 $\mu\mu$ to 282 $\mu\mu$ the results are of similar nature to those found in other photochemical reactions in aqueous solution. In an experiment in which λ was 222 $\mu\mu$ and [HI] was reduced to $0{\cdot}01N$, no iodine formation was detected, i.e. $\gamma = 0$. Since at this low concentration HI is completely ionised in aqueous solution, the absorbing entity is then the I' ion, and it follows that light which is absorbed by I' ions yields no formation of iodine. Warburg and Rump consider that with high concentrations of HI, partial association of the ions takes place and that the photolyte is the undissociated HI molecule. The observed values of γ are thus smaller than the "true" values, especially in the more dilute solutions where the degree of ionisation and the fraction of the light absorbed by I' ions are great. The decrease in the observed values of γ with decreasing concentration of photolyte is thus attributed to the effect of electrolytic dissociation, an effect which also might similarly be present in the photolyses of the chlorplatinic acids and of potassium nitrate. If, on the other hand, Vranek's result that the quantum yield in the photolysis of potassium cobaltioxalate is independent of concentration be correct, this would mean that light is equally effective in decomposing the ion $Co(C_2O_4)_3'''$ and the undissociated molecule, and that his observed values of γ are the " true " ones.

The effect of λ on the observed values of γ in the decomposition of aqueous solutions of HI is, in general, an increase in γ with decreasing wave-length; how the " true " values change is not known. From the fact that the presumed " true " values of γ in the photolysis of potassium cobaltioxalate increase with diminishing λ, Warburg and Rump deem it probable that the same holds for the photo-decomposition of HI in water, and they contrast this behaviour with that found for the same reaction in hexane, for which the change of γ with λ is small and in the other direction. The difference they ascribe to the difference in molecular condition of the photolyte in the two solvents; in water HI is probably hydrated, in hexane it is probably present in the free state.

Table L. shows that with $[HI] = 7{\cdot}5N$ and $\gamma = 207\ \mu\mu$, γ is greater than 2, and the " true " value of γ is greater still. Since on the basis of the mechanism suggested and universally accepted for the photolysis of gaseous HI, the maximum quantum yield is two, Warburg and Rump suggest that in aqueous solutions of HI immediate dissociation into atomic H and I does not follow the quantum process of absorption, but that activated molecules are formed and that one quantum may, in some way, bring about several reactions of the type

$$HI + HI^* \rightarrow H_2 + I_2$$

when the concentration of HI is great.†

Results of interest were obtained by Rudberg (*Z. Physik*, **24**, 247, 1924) in a study of the energetics of the hydrolysis of monochlor- and monobrom-acetic acids. Using light of wave-length 253 $\mu\mu$, the yield in the former reaction is that given by the Stark-Einsten relation. In these experiments the concentration of photolyte was $0{\cdot}5 - 0{\cdot}3N$. With monobromacetic acid, however, at concentrations of $0{\cdot}02 - 0{\cdot}01N$, the quantum yield was but $0{\cdot}35 - 0{\cdot}32$. The yield in this reaction may be increased somewhat by working in neutral or alkaline solution, but owing to the increased velocity of the thermal change accompanying the photochemical reaction the results are less accurate. Rudberg shows that the increased yield caused by increasing the concentration of OH′ cannot be accounted for by the assumption that the reaction is a simple collision reaction between OH′ ions and activated molecules of the brom-compound. It is possible, as pointed out by Allmand (*Trans. Faraday Soc.*, **21,** 446, 1926), that the lower yield with the brom-acid is connected in some way with the much lower concentration of photolyte used.

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† Franck and Scheibe (*Z. physikal. Chem.*, **139**, 22, 1928) suggest an alternative explanation of these effects. The primary process they regard as the ejection of an electron from an iodine ion ($I' + h\nu \rightarrow I + \ominus$), that is, the iodine ion and not the undissociated molecule of HI is taken to be the light-absorbing constituent of the system. In weak solutions, it is assumed that there is a greater probability of this electron being captured by iodine atoms than by hydrogen ions. For more concentrated solutions, however, Debye-Hückel interionic attraction results in each iodine ion being—on the average—in close proximity to more $H^\cdot$ ions than I' ions; hence the probability increases that an electron liberated from an iodine ion will react with a hydrogen ion ($H^\cdot + \ominus \rightarrow H$), with consequent increase in quantum yield. The experimental result that γ may exceed 2 is attributed to the possibility that the energy liberated by the reactions $H^\cdot + \ominus \rightarrow H$ and $H + H \rightarrow H_2$ may be utilised in initiating fresh elementary processes.

Other reactions in aqueous solution associated with low quantum yields are the decomposition of potassium permanganate, the hydrolysis of acetone, and in especial the photolysis of oxalic acid. The first of these reactions was studied by Rideal and Norrish (*Proc. Roy. Soc.*, **103**A, 342, 366, 1923), who followed the course of the decomposition by determination of the potential of an indifferent electrode placed in the solution, and also by spectrophotometric methods. The reaction which occurs on illumination may be written $2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + \frac{3}{2}O_2$; slow combination of alkali with MnO_2 to form manganite, however, follows the photo-reaction. The process follows a unimolecular course at the concentrations employed, and with light of 313 $\mu\mu$* the quantum yield is but 0·5, in spite of the fact that the reaction is exothermic to the extent of 14,000 cal. per gram-molecule. The hydrolysis of acetone, $CH_3 . CO . CH_3 + H_2O \rightarrow CH_4 + CH_3COOH$, in ultra-violet light has, according to Bowen and Watts (*J.C.S.*, **129,** 1611, 1926), a quantum efficiency smaller than 0·2. This result is in marked disagreement with earlier measurements by Henri (*Compt. rend.*, **156,** 1012, 1913), who found 1300 molecules of acetone hydrolysed per quantum of ultra-violet light absorbed. It is probable that the latter's results were vitiated by errors due to vaporisation of acetone from the open quartz cells employed.

Much more work has been done on the third reaction mentioned above, namely, the photolysis of solutions of oxalic acid. Berthelot and Gaudechon (*Compt. rend.*, **152,** 262, 1911; **158,** 1791, 1914), who investigated the action of ultra-violet light on many organic substances, studied the photolysis of oxalic acid both in solution and in the solid state. More recent work on the latter reaction has been carried out by Noyes and Kouperman (*J. Amer. Chem. Soc.*, **45,** 1398, 1923). Dealing with the photolysis in aqueous solutions, the French investigators concluded that the upper limit of wave-length at which decomposition occurs is about 300 $\mu\mu$, and that the primary reaction which occurs is decomposition into formic acid and CO_2. The formic acid, however, may itself be decomposed in two ways,

$$(\alpha)\ H . COOH \rightarrow H_2O + CO$$
$$(\beta)\ H . COOH \rightarrow H_2 + CO_2,$$

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* Visible light has no appreciable action on solutions of potassium permanganate.

the latter reaction only setting in when ultra-violet light of wave-length lower than 250 $\mu\mu$ is present. In the full light of the quartz mercury lamp, the products of decomposition are stated to be only CO_2 and H_2. Allmand and Reeve (*J.C.S.*, **129,** 2834, 2852, 1926), in a recent re-investigation of this reaction as well as of the photolysis of formic acid, have obtained results not in agreement with those of Berthelot and Gaudechon. Employing sensitive micro-analytical methods, they studied the initial stages of the oxalic acid reaction, and confirmed that the primary process is decomposition into formic acid and CO_2. The reaction sets in, however, at wave-lengths as high as 365 $\mu\mu$. They found also that the amounts of CO and H_2 in the gases analysed at the completion of an experiment were small compared with the CO_2, and that the ratio CO : H_2 was unity and independent of the wave-length of the activating light, a result not in accord with the experiments of Berthelot and Gaudechon. They finally concluded that what was analysed as a mixture of CO and H_2 was formaldehyde vapour and that neither CO nor H_2 actually appears as such in the initial stages of the photolysis of oxalic acid. The amount of formaldehyde formed is small, but increases with diminishing wave-length of the activating light. The mechanism of formaldehyde production favoured by the authors is reactions between activated CO_2 molecules (formed in the primary dissociation of oxalic acid) and water—

$$CO_2^* + H_2O \rightarrow H\,.\,CHO + O_2.$$

Determinations of quantum yield were carried out with light of three wave-lengths, 265 $\mu\mu$, 300 $\mu\mu$, and 365 $\mu\mu$. The values of γ obtained with 0·6-0·7M solutions were respectively 0·01, 0·0041, and 0·00094. The effect of frequency on quantum yield in this reaction as in the photolysis of the chlorplatinic acids (Boll) is thus very pronounced. The quantum yield of the photochemical decomposition of oxalic acid in aqueous solution has also been determined by Anderson and Robinson (*J. Amer. Chem. Soc.*, **47,** 718, 1925). They find that for a 0·1N oxalic acid solution in non-homogeneous light whose average wave-length is taken to be 283 $\mu\mu$, the quantum efficiency is but 1/1135.† Allmand and Reeve (*loc. cit.*) estimate from their own results that at this wave-length γ is of the order 1/160, about 7 times greater. It is probable that Anderson and Robinson's figure is much too low, since comparison of their results for another photo-reaction—the decomposition of oxalic acid sensitised by uranyl sulphate—with data obtained by Büchi (*Z. physikal. Chem.*, **111,** 269, 1924) and confirmed by Bowen and Watts (*J.C.S.*, **129,** 1607, 1926) indicates that the values of γ of the American investigators are about 25 times too small. Very discrepant results have been obtained for the quantum yield of this sensitised reaction. While Bowen and Watts and also Büchi found γ to be unity and Anderson and Robinson obtained 1/25, Boll (*Compt.*

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† The figure given in the paper of Anderson and Robinson is 1/1392; the figure in the text is calculated from the data in their table.

rend., **156**, 1891, 1913) found that 50 molecules of oxalic acid disappear for every quantum absorbed. It would seem, however, that in the latter investigation the reaction mixture was exposed to atmospheric oxygen, and that the uranyl salt was playing the part of an oxygen carrier, with the result that the measured change was oxidation according to

$$2H_2C_2O_4 + O_2 \rightarrow 4CO_2 + 2H_2O.$$

In the other work quoted, however, the reaction measured was mainly the (sensitised) decomposition of oxalic acid according to the equation

$$H_2C_2O_4 \rightarrow CO + CO_2 + H_2O.$$

Reverting to the decomposition of pure oxalic acid solutions, Allmand and Reeve (*loc. cit.*) obtained indications in preliminary experiments that the quantum yield increases with increasing dilution of the photolyte. In 0·001M solution, the value of γ found was about 1·7 times that in 0·6M solution. This behaviour is the reverse of that found for other reactions in aqueous solution, for example, the decomposition of KNO_3 and the photolysis of the chlorplatinic acids. The authors suggest in explanation that deactivation of activated oxalic acid molecules takes place on collision with other oxalic acid molecules, hence the observed effect of change in concentration. Alternatively, however, it might be due to change in ionisation of the photolyte with concentration.

The photolysis of aqueous solutions of formic acid was also investigated by Allmand and Reeve. Using either unfiltered light of the quartz mercury lamp or the wave-lengths 280-313 $\mu\mu$, the chief product obtained was carbon dioxide. Small quantities of CO and H_2 were also detected as well as considerable quantities of formaldehyde and other reduction products. The reaction is much more photosensitive than the decomposition of oxalic acid, quantum efficiencies of 1·0 for $\lambda = 300\ \mu\mu$ and 2·7 for $\lambda = 260\ \mu\mu$ being obtained for solutions of concentration 2·4N and 0·113N respectively. The reaction mechanism suggested is as follows. Two primary reactions occur—

$$(\alpha)\ H\,.\,COOH \rightarrow H_2{}^* + CO_2$$
$$(\beta)\ H\,.\,COOH \rightarrow H_2O + CO^*,$$

the rate of (α) being approximately six times that of (β). The deficiency of hydrogen in the final reaction products and the formation of formaldehyde are ascribed to the reaction

$$(\gamma)\ H_2{}^* + H\,.\,COOH \rightarrow H\,.\,CHO + H_2O.$$

The mechanism of formaldehyde formation here postulated is thus different from that assumed in the photo-decomposition of oxalic acid, where it was ascribed to the reaction

$$CO_2{}^* + H_2O \rightarrow H\,.\,CHO + O_2.$$

It receives support from the fact that in an experiment with a dilute solution of formic acid an increased percentage of hydrogen in the final gaseous products was obtained, together with a much diminished yield of formaldehyde. Further, in the same experiment, the ratio $CO : CO_2$ in the products of photolysis was much greater than that obtained from strong solutions of formic acid. This suggests that the carbon monoxide formed in reaction (β) is also activated and able to react with formic acid according to

$$(\delta) CO^* + H.COOH \rightarrow CO_2 + H.CHO.$$

The difference between the quantum efficiencies at 300 $\mu\mu$ and 260 $\mu\mu$ is ascribed to the H_2 or CO formed on absorption of the quantum of the former wave-length not being sufficiently rich in energy to react with formic acid. On the other hand, the value 2·7 for γ at the shorter wave-length might be interpreted as due to the production of short chains. It is suggested that the activated H_2 or CO molecules may in the first stages of deactivation still retain sufficient energy to break up formic acid molecules on collision by the processes

$$\begin{aligned} CO^* + H.COOH &\rightarrow H_2 + CO_2 + CO \\ H_2^* + H.COOH &\rightarrow H_2 + H_2O + CO, \end{aligned}$$

but not sufficient to produce formaldehyde.

Finally, no evidence was obtained in these experiments to support Berthelot and Gaudechon's contention that formic acid decomposes in two different ways above and below 250 $\mu\mu$, with production of CO and H_2O in the former case and of CO_2 and H_2 in the latter. Volmar (*Compt. rend.*, **178,** 698, 1924; **180,** 1172, 1925) calculated from thermochemical data that the threshold frequency at which decomposition of oxalic acid should set in corresponds to $\lambda = 320$ $\mu\mu$, that for the reaction $H.COOH \rightarrow CO_2 + H_2$ to $\lambda = 215$ $\mu\mu$. While these are in agreement with Berthelot and Gaudechon's data, they are not confirmed by Allmand and Reeve. The latter find that the decomposition of oxalic acid takes place with light of wave-length 365 $\mu\mu$ and the photolysis of formic acid into CO_2 and H_2 with light of wave-length 280-313 $\mu\mu$. Further, Volmar's calculations have been criticised by Bowen (*Trans. Faraday Soc.*, **21,** 544, 1926) on the grounds that an incorrect value of the heat of vaporisation of carbon—a magnitude required to calculate the heats of linking C-C and C-H—was employed. Also, as emphasised by Franck (*Z. Elektrochem.*, **31,** 350, 1925), there is no theoretical basis for equating the energy of dissociation of a molecule to the smallest quantum effective in producing the primary dissociation, since—at all events in the case of diatomic molecules—when dissociation occurs as a result of light absorption in a single elementary process, the products are not normal atoms but a normal and an activated atom.

The next reaction to be considered, the photochemical decomposition of chlorine water, has been the object of much attention. Discovered originally in 1785 by Berthollet and a few years later recommended by de Saussure for actinometric purposes, it has since been one of the most studied of all photochemical reactions. The results obtained, which have been summarised by Plotnikow (*Lehrbuch der Photochemie*) and by Mellor (*Inorganic and Theoretical Chemistry*, Vol. II.), have, however, been conflicting in certain respects, and lack of agreement is found between the views of different authors regarding the mechanism and kinetics of the reaction, and even regarding the nature of the reaction products. A definite advance in our knowledge of this photochemical process, as well as of the analogous photodecomposition of hypochlorous acid, would appear to have been made by the recent work of Allmand, Cunliffe, and Maddison (*J.C.S.*, **127,** 822, 1925; **131,** 655, 1927). These authors' determinations of the quantum yield afford a firmer basis for the elucidation of the mechanism of the two processes than the results of the older work. We may now confine our attention to the energetics and mechanism of these reactions, referring the reader for other data to the summaries quoted above as well as to papers referred to by Allmand, Cunliffe, and Maddison (*loc. cit.*). It would now appear to be definitely established from the work of these investigators that both chlorine water and hypochlorous acid yield on insolation HCl, O_2, and $HClO_3$ as sole products. No evidence for the previously reported formation of perchloric acid or of H_2O_2 was obtained. Stoichiometrically, therefore, two processes occur; for chlorine water

$$(\alpha)\ Cl_2 + H_2O \rightarrow 2HCl + \tfrac{1}{2}O_2$$
$$(\beta)\ 3Cl_2 + 3H_2O \rightarrow HClO_3 + 5HCl,$$

and for solutions of hypochlorous acid

$$(\alpha)\ HOCl \rightarrow HCl + \tfrac{1}{2}O_2$$
$$(\beta)\ 3HOCl \rightarrow HClO_3 + 2HCl.$$

The percentage of photolyte which on reaction yields chloric acid is in both cases about 60, and is markedly affected neither by the initial concentration nor by the extent of decomposition nor by the wave-length of the activating light. The ratio of chloric acid to oxygen formed may, however, suffer considerable alteration if electrolytes are present in the insolated solution; this ratio is increased (in both reactions) by the addition of sodium phosphate, lithium sulphate, and sodium sulphate, but is diminished slightly by sulphuric acid and more by the chlorides of lithium and sodium and by hydrochloric acid. Further, it is concluded that in a solution of Cl_2 in water in which the equilibrium $Cl_2 + H_2O \rightleftharpoons HOCl + Cl$ (the Jakowkin equilibrium) is set up, both the chlorine molecule and the HOCl molecule are photosensitive. Measurements of the light absorption of chlorine water show that the molecular extinction coefficient of the solution increases with increasing concentration of chlorine, which fact is readily explained on the basis of the above equilibrium if the molecular extinction of Cl_2 is greater than that of HOCl. An increased extinction of chlorine water is also caused by the addition of LiCl, KCl, and HCl; on the other hand, Li_2SO_4 and Na_2SO_4 effect a diminution in the absorption. Solutions of HOCl have smaller extinctions than those of chlorine; here the absorption is increased by the addition of Na_2HPO_4. This probably indicates the occurrence of the reaction $HPO_4'' + HOCl \rightarrow H_2PO_4' + OCl'$, and that the OCl' ion has a greater extinction than free hypochlorous acid.

The following table gives the results of the determinations of quantum efficiencies. The light employed was non-homogeneous, the values of γ relating to a mean wave-length between 365 and 405 $\mu\mu$. Other experiments showed, however, that the quantum yield is very little dependent on λ, so that the figures given might be taken as applying to $\lambda = 365$ $\mu\mu$, the region of greatest energy absorption in these experiments.

TABLE LI.

Solution.	Initial Conc. of Cl_2 (HOCl).	Duration of Illumination (Hours).	$HClO_3$ Yield (Per Cent.).	Quanta Absorbed ($\times 10^{-20}$).	Molecules Decomposed ($\times 10^{-20}$).	γ.
Cl_2 water	0·0503	41·5	46	14·0	22·2	1·59
,,	0·02725	23·0	62	10·03	20·35	2·03
,,	0·0550	30·0	61	16·35	34·0	2·08
Cl_2 water + 0·004 *N* HCl	0·0405	27·0	56	15·32	6·96	0·45
Cl_2 water + 0·6*N* HCl	0·03775	48·25	—	29·87	1·61	0·054
Cl_2 water + 0·5*N* LiCl	0·0440	46	39	32·88	8·24	0·25
Cl_2 water + 0·33*M* Na_2SO_4	0·0330	26·75	—	14·92	5·36	0·42
HOCl + 0·125*M* Na_2HPO_4	0·05575	69	86	23·4	40·2	1·72

It will be seen that the value of γ for pure chlorine water is about 2·0,† but is much lowered by the addition of HCl, LiCl, and Na_2SO_4, the first of these substances acting as the most efficient retarder of the reaction. The value of the quantum efficiency for the photolysis of hypochlorous acid in the presence of Na_2HPO_4 is slightly less than that obtained for chlorine water. A consideration of these and other results led Allmand, Cunliffe, and Maddison to suggest the following reaction mechanisms for the two cases:—

For Hypochlorous Acid.	For Chlorine Water.
(1) $HOCl + h\nu \rightarrow HCl + O$	(1) $Cl_2, H_2O + h\nu \rightarrow 2HCl + O$
(2) $O + O \rightarrow O_2^*$	(2) $O + O \rightarrow O_2^*$
(3) $HOCl + O \rightarrow HCl + O_2^*$	(3) $Cl_2, H_2O + O \rightarrow 2HCl + O_2^*$
(4) $HOCl + O_2^* \rightarrow HClO_3$	(4) $Cl_2, H_2O + O_2^* \rightarrow HClO_3 + HCl$
(5) $O_2^* \rightarrow O_2$	(5) $O_2^* \rightarrow O_2$

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† The lower value in the first experiment of the table, combined with the low yield of chloric acid, makes it likely that the solution contained some HCl in addition.

There is a close similarity between the two reactions, and this is reflected in the assumed mechanisms. In the case of the chlorine water reaction, the photosensitive reactant is postulated to be, not a definite chlorine hydrate, but a grouping of the two constituent molecules in sufficiently close association. These mechanisms allow of a maximum quantum efficiency of 3, which figure would be associated with 100 per cent. yield of $HClO_3$; if no $HClO_3$ were formed, the maximum value of γ attainable would be 2. If, as appears to be permissible except in the case of dilute solutions, reaction (2) be discarded as occurring only to a negligible extent, it is possible to utilise the data obtained for fractional yield of $HClO_3$ and for γ in each experiment to calculate (α) the fraction of the total number of quanta absorbed which initiate the primary reaction (1), and (β) the fractions of activated oxygen molecules (O_2^*) which react according to (4) and (5) respectively. Analysis of the results of this calculation makes probable the following conclusions:—

(*a*) The efficiency of the primary process in the case of pure chlorine water and perhaps also for hypochlorous acid solutions free from added electrolyte is not far removed from unity.

(*b*) Strong electrolytes, particularly hydrochloric acid, lower to a marked extent this efficiency.

(*c*) HOCl molecules appear to be more efficient as acceptor molecules for activated oxygen than do Cl_2—H_2O complexes. This may account for the non-appearance of a decreased fractional yield of $HClO_3$ from chlorine water on dilution, since the increased velocity of deactivation of O_2^* molecules might be to some extent compensated by the increased degree of hydrolysis of Cl_2.

(*d*) The effect of H_2SO_4 on the relative extents of reactions (4) and (5), i.e. on the percentage formation of chlorate—a slight effect diminishing the rate of reaction (4)—, is attributed to its action in increasing the concentration of Cl_2 by the reaction $HOCl + H^{\cdot} + Cl' \rightarrow Cl_2 + H_2O$. The reverse action of the sulphates of Li and Na is due most probably to removal of $H^{\cdot}$ by the process $H^{\cdot} + SO_4'' \rightarrow HSO_4'$ and consequent increase in the concentration of HOCl. The changes in extinction of the solution and in volatility of chlorine are in agreement with these views.

(*e*) The influence of chlorides on the relative speeds of reactions (4) and (5) is more complex. In addition to a retarding effect on reaction (4) caused by the diminished concentration of HOCl, there appears also to be an opposed effect specific to the cation.

The kinetics of the two reactions are somewhat complicated, but experiments made to determine their apparent order gave results not in disagreement with the above mechanisms. It may be seen that when the reaction follows the course represented by processes (1), (3), and (4), the order will lie between 0 and 1, varying in the usual manner with the extent of absorption of energy. When, however, in dilute solution reaction (2) becomes of greater significance than (3), the apparent order will increase, and may be greater than 1. Yet simple behaviour is in general not to be anticipated, since, during the photolysis, changes may occur in the molecular extinction of the solution and also in k_1, which is a measure of the efficiency of the primary process.

While the above mechanisms account in a satisfactory manner for the observed quantum yields and the percentage amounts of chloric acid formation, they appear to require modification if they are to account for the high temperature coefficient found for the chlorine water reaction. According to Benrath and Tuchel (*Z. wiss. Phot.*, **23,** 66, 1924), this has the value 1·4, which, if substantiated, requires that on increasing the temperature by 20° quantum efficiencies considerably greater than 3—the maximum attainable in terms of the postulated reaction scheme—will obtain.

Similar in many respects to the photo-decomposition of chlorine water (or of hypochlorous acid) is the photolysis of sodium hypochlorite in aqueous solution, a reaction studied by Lewis (*J.C.S.*, **101,** 2371, 1912) and Spencer (*ibid.*, **105,** 2565, 1914), then more completely by Allmand and Webb (*Z. physikal. Chem.*, **131,** 189, 1928). In either reaction, formation of both oxygen and chlorate takes place and the chlorate yield is to a considerable degree independent of the conditions of experiment. Allmand and Webb found, for example, that the fraction of NaOCl decomposing to yield $NaClO_3$ was between 0·40 and 0·53 and was independent of the concentration of the hypochlorite (except at low values of [NaOCl]), of the concentration of free alkali and of Na_2SO_4, and of the light intensity, but increased with increasing frequency of the activating light. The quantum yield (molecules NaOCl decomposed per quantum absorbed) has been determined with light of three wave-lengths—365 $\mu\mu$, 313 $\mu\mu$, and 254 $\mu\mu$. With $\lambda =$ 365 $\mu\mu$, γ was found to be about unity, to be but little influenced by the concentration of NaOCl,† and to be increased somewhat by addition of sodium chloride. With $\lambda = 313$ $\mu\mu$, a quantum yield of 1·2 was obtained, while with $\lambda = 254$ $\mu\mu$, γ rose to 4·7. These results (except the last) are interpreted by Allmand and Webb on the basis of a mechanism exactly similar to that postulated for the photolysis of chlorine water, ClO′ ions now being substituted for neutral Cl_2—H_2O complexes or HOCl molecules. Comparing the two reactions (using wave-length 313 $\mu\mu$ or 365 $\mu\mu$) in the light of this mechanism, the lower values of γ and the smaller chlorate yields in the sodium hypochlorite reaction mean that the efficiencies of both the primary process (1) and the reaction between activated O_2^* molecules and acceptor molecules (process (4)) are less with sodium hypochlorite than with chlorine water. Again, the addition of NaCl causes an increase in γ in the sodium hypochlorite reaction, but the reverse is true for the chlorine water reaction. In terms of the mechanism adopted, this difference is attributed to different actions of NaCl (and of strong electrolytes generally) on the primary process (1) caused by quantum absorption. This result would suggest that when the photolyte is an ion, the efficiency of the primary process is enhanced by strong electrolytes, which—on the other hand—retard the first step in the photolysis of a neutral molecule.

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† Except in very dilute solution when both γ and the chlorate yield are perceptibly diminished.

The maximum quantum yield permitted by the mechanism above given is 3; it is clear that the quantum yield of 4·7 obtained with short wave ultra-violet light ($\lambda = 254\ \mu\mu$) is irreconcilable with the scheme. Allmand and Webb therefore suggested that additional secondary reactions take place when the originally absorbed quanta are sufficiently large, and they advanced a modified scheme based on this standpoint (cf. *Z. physikal. Chem.*, **131,** 189, 1928).

In the photolysis of chlorine water and of HOCl, added chlorides exert a retarding effect. The same behaviour has also been observed in the case of other photochemical reactions, such as the photolysis of uranyl formate (Hatt, *Z. physikal. Chem.*, **92,** 513, 1918) and the reaction between $HgCl_2$ and potassium oxalate (Roloff, *Z. physikal. Chem.*, **13,** 94, 1894). It is not known whether the same effect applies to the photo-reaction between I_2 and $Fe^{\bullet\bullet}$ in aqueous solution, in which case, however, the influence of ionic activities on the photochemical stationary state is of interest (see p. 389). Light (of wave-length 550-650 $\mu\mu$) displaces the equilibrium position of the process

$$2Fe^{\bullet\bullet} + I_2 \rightleftharpoons 2Fe^{\bullet\bullet\bullet} + 2I'$$

towards the right-hand side. The photosensitive constituent is iodine (or the I_3' ion), and it was shown by Rideal and Williams (*J.C.S.*, **127,** 258, 1925) that one quantum of absorbed radiant energy causes the disappearance of one molecule of iodine under the conditions of their experiments. The addition of KCl increases the velocity of attainment of the "dark" equilibrium, so that the velocities of the two opposing thermal reactions are increased. It does not appear unlikely that the velocity of the photochemical reaction is also increased by the Cl' ion, but experiments to test this have not yet been carried out. Another reaction in which the effect of added electrolytes has been determined is the photochemical decomposition of potassium persulphate (Morgan and Crist, *J. Amer. Chem. Soc.*, **49,** 960, 1927). Sulphuric acid, potassium sulphate, and potassium hydroxide all exert a retarding effect on the velocity, and since the light absorption remains unaltered in the presence of the substances, the quantum yields are in each case reduced. The effects in these cases do not appear to be specific; all three electrolytes retard the reaction to an equal extent which may be represented by the hyperbolic equation $y = \frac{x}{a + bx}$, in which y = velocity, x = equivalent concentration of electrolyte, and a and b are constants. It would appear, therefore, that the similarity of the effects for these entirely different electrolytes indicates a common cause, but the nature of the deactivation process which must be assumed is as yet obscure.

To conclude our survey of reactions effected in aqueous solution, two further examples will be discussed which are of interest in relation to the I_2—$K_2C_2O_4$ reaction (p. 451) and to the bromination of stilbene and cinnamic acid (p. 454). The cases referred to are the reaction between iodine and potassium nitrite and the oxidation of alcohol by bromine, both in aqueous solution. The first of these reactions, which takes place according to the equation

$$KNO_2 + I_2 + H_2O \rightarrow KNO_3 + 2HI,$$

has been studied by Banerji and Dhar (*Z. anorg. Chem.*, **134**, 172, 1924), Mukerji and Dhar (*Z. Elektrochem.*, **31**, 621, 1925), and Berthoud and Berger (*Helv. Chim. Acta*, **11**, 354, 1928). Dhar determined the temperature coefficients of the "light" and "dark" reactions and also the quantum yield of the former, but, according to Berthoud and Berger, the results are vitiated by a faulty analytical method. The latter workers studied in some detail the kinetics of the "light" reaction, employing solutions containing excess of KI and of KNO_2 and also Na_2HPO_4 and NaH_2PO_4 to keep the reaction mixture neutral. At temperatures lower than 45° the rate of the "dark" reaction was found to be negligible, and the photo-process could be studied unattended by complications due to the thermal reaction. The results obtained when the radiation was feebly absorbed (yellow light) are well expressed by the equation

$$-\frac{d[I_2]}{dt} = k'\frac{I_0[I_{total}][KNO_2]}{[KI]\{[KI] + k''[KNO_2]\}},$$

in which I_0 is the light intensity and $[I_{total}]$ the concentration of titrable iodine, which, under the conditions employed (excess of KI), is practically equal to $[I_3']$. (With blue light, which is strongly absorbed, the reaction velocity is proportional to I_0 but is independent of the concentration of iodine.) It will be observed that this kinetic equation is entirely different from that found in the I_2—$K_2C_2O_4$ reaction, and a different type of reaction mechanism must be assumed. Berthoud suggests the following series of reactions, in which the resultants of the primary process interact first not with KNO_2 but with water :—

(1) $I_2 + h\nu \rightarrow 2I$
(2) $2I + H_2O \rightarrow HIO + I' + H^{\cdot}$
(3) $HIO + I' \rightarrow I_2 + OH'$
(4) $HIO + NO_2' \rightarrow NO_3' + H^{\cdot} + I'$
(5) $I_2 + I' \rightleftharpoons I_3'$.

The OH' ions formed in (3) combine with $H^{\cdot}$ ions resulting from (2) and (4), and the excess of the latter are removed by the phosphate buffer. Equation (1) involves the assumption that only I_2 molecules and not KI_3 molecules or I_3' ions are activated by light. With this assumption we obtain, when the light is weakly absorbed,

$$[HIO] = \frac{k_1 I_0[I_2]}{k_3[I'] + k_4[NO_2']},$$

and since from (5) we have $[I_2][I'] = K[I_3']$, it follows that

$$[\mathrm{HIO}] = \frac{k_1 K I_0 [I_3']}{[I']\{k_3[I'] + k_4[\mathrm{NO_2'}]\}}$$

and that

$$+\frac{d[\mathrm{NO_3'}]}{dt} = -\frac{d[I_2]}{dt} = k_4[\mathrm{HIO}][\mathrm{NO_2'}] = \frac{k_1 k_4 K I_0 [I_3'][\mathrm{NO_2'}]}{[I']\{k_3[I'] + k_4[\mathrm{NO_2'}]\}},$$

in formal agreement with the experimentally determined velocity. It is clear that this scheme is not a "chain" mechanism; in fact, smaller quantum yields than unity are to be anticipated owing to removal of the active agents (HIO molecules) by reaction (3). The actual value of the quantum yield naturally depends on the experimental conditions; in one case, Berthoud and Berger obtained a value of about 0·05.

The differences between the kinetics of this reaction and of the $K_2C_2O_4$—I_2 reaction are of some theoretical interest, and, as emphasised by the mechanisms advanced by Berthoud, they would seem to be dependent on the fact that water is a reactant in the one process but not in the other. Yet it is not clear how the assumption of process (2) in the KNO_2—I_2 reaction as the reaction involving water is to be brought into line with the scheme postulated for the $K_2C_2O_4$—I_2 reaction. Examination of the two mechanisms shows that the following four reactions are suggested for iodine atoms :—

(*a*) $I + I \rightarrow I_2$
(*b*) $I + I + H_2O \rightarrow HI + HIO$
(*c*) $I + I + I' \rightarrow I_3'$
(*d*) $I + C_2O_4'' \rightarrow I' + C_2O_4'$.

In order to satisfy the experimental data for the $K_2C_2O_4$—I_2 reaction, it is necessary to presume that the velocity of (*d*) > velocity of (*c*) > velocity of (*b*); on the other hand, the scheme for the KNO_2—I_2 reaction requires that the velocity of (*b*) > velocity of (*c*). One or other of the reaction mechanisms thus requires modification.

The second photo-reaction briefly to be considered is the oxidation of alcohol by bromine in aqueous solution, a process studied by Berthoud and Beraneck (*J. Chim. phys.*, **25**, 28, 1928). The reaction is complex and takes place in two stages :—

(*a*) $CH_3 . CH_2OH + Br_2 \rightarrow 2HBr + CH_3 . CHO$
(*b*) $CH_3 . CHO + Br_2 + H_2O \rightarrow 2HBr + CH_3 . COOH$,

the first of which is the slow process whose velocity is measured, the second being fast in comparison. Oxidation of alcohol by bromine also takes place in the dark, the thermal rate being proportional to the product of the concentrations of bromine and alcohol, and inversely proportional to the concentration of KBr raised to a power less than unity. The kinetics of the photo-process is, however, different, since the velocity, when the light employed is feebly absorbed, is reproducible by an expression of the type

$$-\frac{d[\mathrm{Br_2}]}{dt} = k \cdot \frac{I_0^{\,x} \cdot [\mathrm{Br_2}]^y \cdot [\mathrm{C_2H_5OH}]^z}{[\mathrm{KBr}]^w},$$

in which x and y are exponents somewhat greater than 0·5, z varies between 0·5 and 1·0, and w is of the order 0·5. The quantum yield under the conditions employed by Berthoud and Beraneck was less than unity. It is naturally not yet possible to interpret this complex kinetic behaviour, which may, perhaps, be attributed to the fact that two *net* processes ((*a*) and (*b*) above) are taking place, and also to the fact that alcohol-water mixtures embracing a somewhat large variation in alcohol content were employed. Yet from the fact that the reaction rate is nearly proportional to the square root of the absorbed energy, one may infer that dissociation of bromine atoms is the primary process, and that probably this is succeeded by reactions such that the transformation of alcohol into aldehyde involves at least two stages. Berthoud suggests the reaction

$$\mathrm{C_2H_5OH + Br \rightarrow C_2H_5O + HBr}$$

followed by

$$\mathrm{C_2H_5O + Br_2 \rightarrow C_2H_4O + HBr + Br}$$

and

$$\mathrm{Br + Br \rightarrow Br_2}$$

or by

$$\mathrm{C_2H_5O + Br \rightarrow C_2H_4O + HBr},$$

but points out that, to explain the retarding action of KBr (which does not influence the photo-oxidation of oxalic acid by bromine), one has probably to assume that HBrO is the active oxidising agent, a hypothesis similar to the one employed in interpreting the $\mathrm{KNO_2}$—$\mathrm{I_2}$ reaction.

Reactions in Non-Aqueous Solution.—There yet remain for discussion a few reactions effected in non-aqueous solution. The first of these is the photo-chlorination of toluene studied by Book and Eggert (*Z. Elektrochem.*, **29,** 521, 1923). In order to eliminate the spontaneous thermal reaction between $\mathrm{Cl_2}$ and toluene, the reaction was investigated at a temperature of − 80° C. The process is still a complicated one, however, since in addition to a substitution reaction yielding chlortoluene or benzylchloride, an addition of chlorine to the unsaturated toluene molecule occurs. In the later stages of the reaction the second of these processes becomes of less importance, and the reaction measured is substantially a substitution reaction which most probably takes place in the side chain. An approximate determination yielded the high value of 27 for the quantum sensitivity, so that some kind of chain mechanism must be postulated. Experiments were also carried out to determine the nature of the action of small quantities of iodine as a " chlorine-carrier." In the presence of iodine the dark reaction occurs even at − 80°, in certain cases only after an induction period. It was proved, however, that iodine does not act as a photosensitiser for the reaction between chlorine and toluene; its action is solely that of a catalyst to the dark reaction, possibly by formation of intermediate compounds such as ICl and ICl_3. The action of I_2 on the analogous photo-bromination of toluene has been investigated by Bruner and Czarnecki (*Bull. Acad. Sci. Cracow*, p. 516, 1910). The reaction is a very complicated one and reproducible results are obtainable with difficulty. The process is strongly retarded by traces of oxygen, which is, however, consumed in the course of the reaction with the production of a positive catalyst. The latter substance is the cause of the observed photochemical after-effect in this case, i.e. the non-cessation of the reaction on cutting off the illumination. In the presence of small quantities of iodine reproducible results could be obtained. The reaction velocity now becomes independent—within certain limits—of the oxygen content of the system, and no after-effect is found. Bruner ascribed the action of iodine in this case to its removing oxygen with formation of oxides of iodine, but according to Stüssel * this is not correct. The stabilising and probably retarding action of iodine on this reaction remains unexplained.

We have previously discussed two cases of isomerisation reactions, namely, the reciprocal transformations of maleic and fumaric acids in aqueous solution and the bromine-sensitised conversion of the ester of maleic acid into fumaric ester in CCl_4 solution. A third example of such a type of reaction is the transformation into *o*-nitrosobenzoic acid of *o*-nitrobenzaldehyde, when subjected—either in the solid state or in solution—to violet or ultra-violet light. The characteristics of the process in liquid solution were studied by Weigert and Kummerer (*Ber.*, **46**, 1207, 1913), and the quantum yield more recently by Weigert and Brodmann (*Trans. Faraday Soc.*, **21**, 453, 1926). The latter find that in acetone solution γ has the value of 0·5 at the three wave-lengths 366 $\mu\mu$, 405 $\mu\mu$, and 436 $\mu\mu$, a quantum sensitivity somewhat higher than the value (0·1) calculated by Bodenstein in 1913 from the data of Weigert and Kummerer. The reaction appears to be a straightforward one, only the normal optical effect of variation of concentration on the reaction velocity being found. In order to account for the observed quantum yield, a specialised theory was introduced by Weigert and Brodmann. They reject as untenable the hypothesis that a molecule of nitrobenzaldehyde must absorb two quanta in order that reaction may ensue, as also the assumption that reaction only occurs on collision of two activated molecules. Instead, they postulate that in the primary absorption of the quantum a definite directive effect is present, and that isomerisation occurs only when the direction corresponds with the direction of the link between the nitro and aldehyde groups of the absorbing nitrobenzaldehyde molecule. Absorption of light causes the passage of an electron to the nitro group from the aldehyde group, but the reaction—the transfer of an oxygen atom from the nitro group—takes place only when the electric vector of the incident radiation corresponds with the connecting direction between these two groups. The orientation of nitrobenzaldehyde molecules in solution is a random one, but for simplicity they may be considered as divided into three classes oriented at right angles to each other. An incident plane-polarised ray will not be absorbed at all by the class of molecules in which the direction of the connecting line between the nitro and aldehyde groups is the same as the direction of the incident light; it will be effectively absorbed by that class of molecules in which the connecting line is in the same direction as the electric vector of the radiation, but not effectively absorbed when the connecting line is co-directional with the magnetic vector. Therefore, of the molecules which absorb only one half can be chemically changed. The same is true for ordinary light, which can be regarded as polarised in all directions. This interesting theory—in which for the first time is assumed a vector action of light on the unconstrained molecules in a solution—has been criticised by Bowen (*Trans. Faraday Soc.*, **21,** 523, 1926), while Franck (*ibid.*, **21,** 581, 1926) believes that deactivation and dissipation of energy by collision cause the low quantum yield in this case.

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* *Diplomarbeit*, Hannover, 1920. (Quoted by Thon, *Fortschritte der Chem.*, **18**, 705, 1926.)

The last reaction to be considered is the polymerisation of anthracene. We have seen (in Chapter VII.) that photo-equilibria between anthracene and dianthracene are established when solutions of anthracene in phenetol and in other hydrocarbons are subjected at high temperatures to ultra-violet light. The measurements of Luther and Weigert show that in all solvents used and at all temperatures the rate of photo-polymerisation increases with increasing concentration of anthracene, even after light absorption is complete. The reaction velocity reaches a limiting value, however, at a concentration of anthracene of about 0·1 normal; increase of [A] above this value is unattended by further change in the rate. These facts suggest the following simple mechanism:—

$$(1)\ A + h\nu \rightarrow A^*;\ (2)\ A^* + A \rightarrow D;\ (3)\ A^* \rightarrow A.$$

This yields

$$\frac{d[D]}{dt} = \frac{k_1 E_{abs}[A]}{[A] + k_3/k_2}.\dagger$$

When [A] is sufficiently great k_3/k_2 may be neglected in comparison with it, and the rate of reaction becomes

$$\frac{d[D]}{dt} = k_1 E_{abs},$$

i.e. the quantum yield $\left(\frac{\text{molecules dianthracene formed}}{\text{quanta absorbed}}\right)$ of the process should be unity. This prediction in regard to the value of γ is not in serious disagreement with the approximate calculations made by

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† A = Anthracene; D = dianthracene; E_{abs} = energy absorbed.

Bodenstein and based on the measurements of Luther and Weigert, but the recent and more exact work of Weigert and Jäckh (*Naturwiss.*, **15,** 124, 1927) indicates that the limiting value of γ at high anthracene concentrations is only 0·25. Experiments were carried out with boiling solutions of anthracene in benzene, in toluene, and in xylene, and the results agreed with those of the older work in respect of the absence of influence of solvent or of temperature on reaction velocity and also in respect of the effect of concentration of anthracene. The significant observation was made, using light of wave-length 366 $\mu\mu$, that the fluorescence of anthracene solutions, which decreases markedly as the concentration of anthracene is increased, practically disappears at the same concentration as that at which the reaction rate (or γ) reaches its limiting value, and, generally, that the fluorescence is inversely proportional to the photochemical yield. Weigert and Jäckh have advanced the following mechanism to account for the smaller limiting yield (0·25) than that predicted by the simple collision hypothesis mentioned above:—

(1) $A + h\nu \rightarrow A^*$
(2) $A^* + A \rightarrow A + A_{III}$
(3) $A^* \rightarrow A +$ fluorescence
(4) $2A_{III} \rightarrow D$
(5) $A_{III} \rightarrow A.$

Here, A_{III} is an anthracene molecule in an activated state different from that of A^*. Reaction (5), the spontaneous deactivation of this isomer, is thus a reaction which diminishes the quantum yield, but apart from this the maximum value of γ is 0·5 since in (4) two activated molecules are assumed necessary to produce one dianthracene molecule. The mechanism is not a satisfactory one, however, since it follows from it that increase of light intensity should be accompanied by an increase in quantum yield. Weigert and Jäckh, however, have themselves shown that a ten-fold increase in the light intensity has no effect on the value of γ.

SUMMARY AND GENERAL DISCUSSION.

In the foregoing pages, theories of the mechanisms of the chief photochemical reactions have been discussed—theories which in the main have been based on experimental determinations of quantum yields. Sensitised reactions have been reserved for a later Chapter, as has also the hydrogen-chlorine reaction. For sensitised reactions Einstein's Law is naturally inapplicable, since the absorbing molecule does not disappear as a result of the reaction. A glance at Tables XL.-XLII. will show, however, that in the sensitised reactions so far investigated the values of the quotient $\frac{\text{molecules reacting}}{\text{quanta absorbed}}$ are in the majority of cases equal to or greater than unity, so that in such processes the yield per unit of absorbed energy is at least on the average not less than in the reactions considered above.

Influence of Wave-Length on Quantum Yield.—One of the best tests of the Stark-Einstein Law is undoubtedly the determination of the quantum efficiencies of photochemical processes employing light of different frequencies. In terms of Warburg's nomenclature, the photo-equivalent relation predicts that

$$p = \frac{\lambda}{28443} \, \frac{\text{moles}}{\text{cal.}},$$

when λ is expressed in microns (μ). For a given quantity of absorbed energy, therefore, the extent of reaction should be proportional to λ. Experiment is in striking agreement with theory in the cases of the photochemical decomposition of HI (at the three wave-lengths 207, 253, and 282 $\mu\mu$) and of HBr (at 209 and 253 $\mu\mu$), and though accurate measurements of photochemical yield are difficult to obtain, these results are to be regarded as strong support from the chemical side that absorption does occur in quanta. Agreement between theory and experiment obtains also in the transformation of *o*-nitrobenzaldehyde,* the decomposition of AgBr in gelatine emulsions, and the photochemical reaction between $Fe^{\cdot\cdot}$ ions and I_3' ions,† while in the reciprocal transformations between maleic and fumaric acids and in the photo-decomposition of chlorine water (and HOCl solutions) the variations of γ with λ are not large and lie possibly within the experimental error. These, however, appear to be the only examples of photo-reactions so far investigated in which ϕ (the effective photochemical equivalent) increases with increasing λ; in most cases ϕ is either independent of the wave-length or (more generally) decreases with increasing wave-length.

This failure of the Einstein relation may in some cases be due to a change in the nature of the primary process in passing from one wave-length to another; in the majority of instances it appears to be connected with the factors operative in producing low quantum yields. Such factors are more likely to exert a greater effect the lower the frequency of the activating light. The two chief reasons for low quantum yields are: (*a*) all absorbing molecules do not succeed in reacting because deactivational processes are operative before reaction, and (*b*) all absorbing molecules do not gain energy sufficient to enable them to react. The first of these explanations was employed by Warburg (*Z. Elektrochem.*, **26,** 54, 1920) to account for the diminution of ϕ with increasing λ in the case of the photochemical formation of ozone, and has since been applied to many other processes. The deactivating processes under consideration may, perhaps, be divided into two groups —(α) a "field effect" by neighbouring molecules on the absorbing molecule, (β) deactivation by collision—though it is not definitely established that process (α) is a deactivation in the sense that (β) is. The " field effect " is made manifest by the broadening of an absorption line or band when the concentration of absorbing material is increased or when non-absorbing substances are added (cf. for example the broadening of the mercury 2536·7 Å line in the presence of helium or argon). Now it is conceivable that in certain cases a consequence of this " damping " effect is that a significant fraction of the absorbed energy passes into the non-absorbing molecule, and that the residue left in the molecule of photolyte is insufficient to raise it to the critical energy level necessary for the particular photo-reaction to take place. On the other hand, for deactivation by collisions of the second kind, we assume that the absorption process is confined to the absorbing molecule, which afterwards loses some or all of its excess energy on collision. In dilute gaseous systems deactivation must naturally be attributed to these collisional effects ; in the liquid state it is at least plausible to presume that the " field effect " may be of significance. In either case, however, it is to be expected that deactivation will be the less marked the greater the frequency of the activating light since, owing to the larger quantum absorbed, the greater becomes the probability that the quantity of energy remaining in the photolyte molecule is sufficient to enable it to react. Weigert (*Z. Elektrochem.*, **23,** 357, 1917) has advanced similar considerations. He emphasises the view that in actual photochemical processes (as distinct from ideal limiting cases) the unit which absorbs the quantum of energy is to be regarded not as a single molecule but as " an optically coupled complex," and that the elementary process causes changes in the whole of the complex.

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* Ornstein (*Trans. Faraday Soc.*, **21,** 517, 1926), however, detects a systematic variation of γ with λ in Weigert's data for this process.

† Kistiakowsky (*J. Amer. Chem. Soc.*, **49,** 976, 1927) finds quantum yields of unity for this reaction at the three wave-lengths 546, 436, and 366 $\mu\mu$.

The other reason for the general non-validity of the Einstein relation between ϕ and λ is that all absorbing molecules may not be activated in the sense that they are able to react. Tolman (*J. Amer. Chem. Soc.*, **45,** 2285, 1923) has pointed out that the chance of a molecule absorbing radiant energy sufficient to bring it to a given energy level depends not only on the frequency and the energy density of the radiation, but also on the internal condition or quantum state of the molecule at the instant it receives the illumination. Now it is possible that molecules in the different quantum states may be able to absorb light of approximately the same frequency, but that, of the molecules which absorb, only those originally in the higher quantum states gain enough energy to raise them to the " reactive " level. The remainder, though absorbing, do not react. An increase of frequency in the incident radiation (assuming it still capable of being absorbed by the same quantum states) would result in a larger proportion of the absorbing molecules being brought to the reactive condition, as some of the lower quantum states would now gain sufficient energy. These considerations would thus be in agreement with the fact that the quantum efficiencies of many photochemical reactions tend to increase with increasing frequency of the light. The fraction of the molecules initially in higher quantum states increases rapidly with increasing temperature. It therefore follows that reactions to which these views are applicable should have low quantum efficiencies and high temperature coefficients, which will decrease as the temperature is increased, γ simultaneously tending towards the value unity. Allmand (*Trans. Faraday Soc.*, **21,** 438, 1926) has tested the available data for such a relation between temperature coefficient and quantum yield, but without success, probably owing to the obscuring influence of secondary processes.

In processes in which high quantum yields prevail, the same decrease in γ with increasing λ is also encountered. The effect may in certain cases be plausibly ascribed to differing reaction possibilities of the excited molecule. An example is afforded in the theory advanced by Kornfeld (*Z. wiss. Phot.*, **21,** 66, 1921) for the mechanism of the photo-decomposition of H_2O_2 in aqueous solution. It is suggested that primarily activated H_2O_2 molecules may react in two different ways according to the extent of activation. One of these reactions—available only to highly activated molecules—is the start of a chain, the other not. Higher quantum yields will thus be obtainable with short wave light. Considerations of an analogous nature have been applied by Allmand and Reeve (*J.C.S.*, **129,** 2834, 1926) to the photo-decomposition of formic acid. In another reaction exhibiting high quantum yields—the bromine-sensitised conversion of maleic ester to fumaric ester—the effect of variation of wave-length has been attributed not to differences in the course of reaction but to differences in the efficiency of the primary process, the formation of bromine atoms. Similarly, to account for the " radiochemical yield " in the H_2—Cl_2 reaction being twice as great as the quantum yield, Lind and his co-workers assumed a difference in the efficiencies of the reactions forming chlorine atoms in the two cases.

As has been indicated, the " rule " in photochemical reactions is that photosensitivity (defined as amount of reaction per unit of absorbed energy) increases with increasing frequency of radiation, the few exceptions being those reactions which obey Einstein's Law at each wave-length and the one or two cases in which there is even a small increase in the quantum efficiency on raising the wave-length (e.g. the photolysis of HI in hexane). There are, however, cases in which the photosensitivity of the absorbing substance to radiation comprised within one absorption band decreases (and indeed drops to zero) when shorter wave radiation comprised within another band is employed. Such are found in the work of Henri and Wurmser (*Compt. rend.*, **156,** 230, 1913) and of Henri and Bielecki (*ibid.*, **155,** 456, 1912) on the photochemical susceptibility of organic acids, aldehydes, and ketones. These workers define photochemical susceptibility as the quantity of photolyte transformed per unit of energy *incident on the system*. The variation with wave-length of the sucesptibility so defined will naturally be largely dependent on the absorption spectrum of the photolyte, but it is clear that if it so happens that photosensitivity (as defined above) is independent of λ, the curves obtained by plotting (*a*) absorption spectrum and (*b*) photochemical susceptibility against wave-length will be coincident if appropriate units are employed. The results obtained by Henri and Wurmser for the case of acetaldehyde (which may decompose into $CH_4 + CO$) are shown in Fig. 45, from which it is seen that while for wave-lengths down to 230 $\mu\mu$ the curves for susceptibility and absorption more or less coincide, for lower wave-lengths the absorption rises rapidly while the photochemical susceptibility remains almost nil.

The absorption band whose maximum is in the region of 280 $\mu\mu$ is due, according to Henri, to absorption by the CO group of the acetaldehyde molecule, while the absorption in the extreme ultra-violet is ascribed to the methyl group. It would appear, therefore, that light absorbed by the CH_3 group does not cause decomposition of acetaldehyde, while the longer wave-lengths absorbed by the CO group are effective. The existence of two types of absorption bands is illustrated by this case—thermal absorption and photochemical absorption. With the former, the absorbed energy is entirely converted into heat; with the latter, chemical transformation occurs. As a rule, "thermal bands" are situated on the long-wave side of "photochemical absorption bands"; the acetaldehyde case, however, forms an exception.

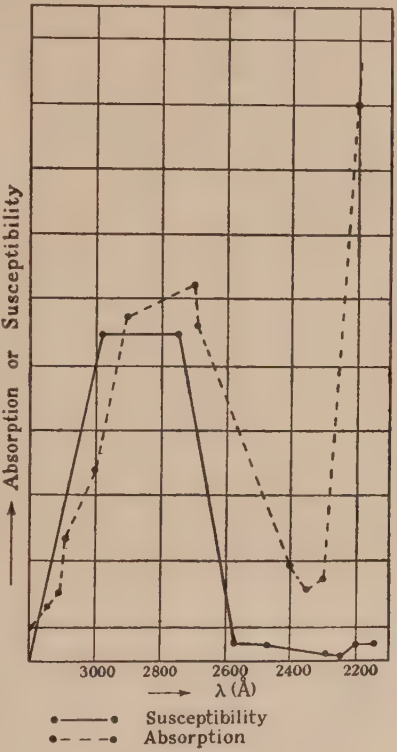

FIG. 45.

The view may thus be accepted that in spectral regions fairly widely separated the absorption may change in character, owing either to the fact that what is energetically possible with one frequency may not be with the other, or to a change in the " degree of freedom " into which the significant part of the absorbed energy goes. In the older work (which has been summarised by Allmand, *Chem. Soc. Ann. Reports*, **22**, 339, 1925), there was a tendency to postulate that the two types of absorption—photochemical and thermal—co-exist even over a narrow region of the spectrum, a theory advocated particularly by

Plotnikow (cf. *Lehrbuch der Photochemie*, Berlin, de Gruyter and Co., 1920). Similar views have also been advanced by Winther and Oxholt-Howe (*Z. wiss. Phot.*, **14,** 196, 1913) as a result of work on the photo-decomposition of ferric salts of organic acids ; they suggested that the absorbing substance (ferric oxalate, tartrate, etc.) is present in two forms, one of which absorbs "thermally," the other "photochemically." While in such cases as this, in which the absorption coefficient varies with the concentration of photolyte, it may formally be allowable to make a classification of this kind, it is not apparent that anything is thereby gained unless some attempt be made to indicate the nature of the different types of absorbing molecules and, if possible, to determine their concentrations by methods other than those dependent on light absorption. Among the suggestions which have been made to account for observed deviations from Beer's Law in solution are polymerisation, dissociation, ionisation, and solvation, and doubtless effects—more or less pronounced—of these types must often play an important part in photochemical reactions in the liquid state. In other cases, in which the observed phenomena should be attributed to "physical" rather than to definite "chemical" effects, much more detailed knowledge of absorption spectra in solution than that at present available is necessary before the subject can usefully be discussed.

The results obtained by Henri and Wurmser (see above) for the photolysis of acetaldehyde illustrate the fact that a substance may occasionally be less reactive after absorbing a large unit of energy than after the absorption of a smaller unit. Somewhat similar behaviour has also been noted by comparison of a photo-reaction with the same process effected thermally. Thus, according to W. C. M. Lewis (*J.C.S.*, **113,** 471, 1918), thermal reaction between hydrogen and iodine occurs as a result of every collision in which the colliding molecules of H_2 and I_2 possess between them energy equivalent to about 40,000 cal. per mole. As shown by Bowen (*Trans. Faraday Soc.*, **21,** 543, 1926), however, no combination occurs when a mixture of hydrogen and iodine is subjected to blue light whereby the iodine receives an energy of activation equivalent to 50,000 cal. per mole. Here the smaller thermal activation is more favourable for reaction than the larger photoactivation which is utilised in producing iodine atoms. In a similar way, the thermal energy of activation necessary for the bimolecular reaction $2N_2O \rightarrow 2N_2 + O_2$ is about 55,000 cal., yet no decomposition of N_2O occurs if to this gas be added some bromine (or N_2O_4) and the system be exposed to violet light, for which the value of $1/p$ (cf. p. 421) is greater than 55,000 cal., and which by a conceivable process of photosensitisation might be utilised in decomposing N_2O.

Closely connected with the relation between γ and λ is the question whether or not *threshold frequencies* exist for photochemical reactions, i.e. whether there exists an upper limit of wave-length above which the quantum yield rapidly drops to zero. According to prevailing theories of photochemical reactions, one would anticipate that before it is in a position to react, the absorbing molecule must be raised to a certain critical energy level. For systems at ordinary temperatures, therefore, in which practically all the molecules are in the lowest quantum state, the *minimum* frequency which must be absorbed for reaction to follow should be given by the relation $N_0 h\nu_{\text{min.}} = q$, where q is the critical energy per mole. If, therefore, q can be otherwise estimated, $\nu_{\text{min.}}$ may be calculated, or if $\nu_{\text{min.}}$ can be experimentally observed, q can be determined. There is, however, no case of a photochemical reaction for which a limiting frequency has been experimentally detected, i.e. for which on increasing the wave-length the quantum yield suddenly falls to zero. The paucity of such data may be due largely to the fact that the absorption coefficient of the photolyte very frequently decreases with increasing wave-length and has become practically immeasurable before the threshold (if one exists) is reached. For example, the ultra-violet absorption of HBr at ordinary pressures practically ceases in the neighbourhood of 264 $\mu\mu$ (corresponding to $\frac{1}{p} = 108{,}000$ cal.); the activating quantum at this wave-length is still greater than the energy necessary (95,000 cal.) to dissociate HBr into Br atoms activated to the extent of 10,500 cal. per mole and H atoms ($HBr + h\nu \rightarrow H + Br^*$). This case also illustrates that methods of estimating q from energies of linking (heats of dissociation) rest on a somewhat doubtful basis. Following Warburg, certain investigators have attempted to calculate threshold frequencies by equating q, the critical energy level, to the energy necessary to dissociate the absorbing molecule into smaller non-activated molecules or into normal atoms. As the case of HBr shows, this is not justified; the heat of dissociation is not necessarily simply related to the minimum energy required for the molecule to become chemically reactive, neither is the latter quantity necessarily related to some observed lower limit of absorption, whose position of course depends on the sensitiveness of the experimental methods employed. From this point of view, Bowen (*Trans. Faraday Soc.*, **21,** 543, 1926) has criticised attempts made by Job and Emschwiller (*Compt. rend.*, **179,** 52, 168, 1924) and by Volmar (*ibid.*, **178,** 697, 1924) to calculate thresholds for the photolysis of certain organic compounds. It has also been shown by Allmand and Reeve (*J.C.S.*, **129,** 2852, 1926) that Volmar's estimates for the threshold wave-lengths of the decomposition of oxalic acid and of formic acid are not confirmed experimentally.

At present we have no certain method of linking chemical activation with physical activation, though developments of the theory of band absorption—especially of diatomic molecules—should eventually lead to clearer insight into these matters. It should be noted, however, that—except for the simplest photochemical reactions—an interpretation of the spectrum of the photolyte will alone not be sufficient to predict a "threshold." Many photochemical reactions are reactions between activated molecules and acceptor molecules; the "threshold" can then vary markedly according to the nature of the acceptor molecule. Also, for a given reaction the threshold might vary appreciably with variation in the experimental conditions, particularly on altering the temperature or the solvent.

Reactions with Low Quantum Yields.—According to Bowen and Watts (*J.C.S.*, **129,** 1611, 1926), about 65 per cent. of the reactions so far investigated have quantum yields approximately equal (within a factor of 3) to those demanded by Einstein's Law, 20 per cent. have higher yields, and the remaining 15 per cent. lower yields than those predicted. We have seen that the generally available explanation of low yields is deactivation of the excited molecules by collision, with degradation of internal energy into heat. The best evidence for such a type of deactivation is furnished by experiments on resonance radiation and fluorescence; the evidence from data yielded by photochemical studies is not unequivocal, as in most cases disturbing effects due to causes of another nature may be present. Consequently, satisfactory knowledge of the probability of transfers of energy on collision of activated particles is available only for simple bodies such as the elements and diatomic molecules. The available data demonstrate—as might have been anticipated—that the probability of loss of energy from an excited atom or molecule on collision with a foreign atom or molecule depends on the specific nature of both colliding particles. If, for example, we compare the efficiencies of nitrogen and hydrogen in deactivating (1) activated Hg atoms and (2) activated Na atoms, the order is quite different in the two cases. The rules governing energy transfers in such comparatively simple systems yet remain unformulated. Until this is done, little progress is to be anticipated in systematising the data for the more complicated systems investigated photochemically.

Stern and Volmer (*Z. wiss. Phot.*, **19,** 275, 1920) suggested a qualitative rule that might be expected to apply to the effect of non-reactant gases on a photochemical gas reaction. This was that the more electronegative the added gas, the greater should be the degradation of energy on collision with the activated molecule, with corresponding greater diminution in quantum yield. The well-known retarding influence of the strongly electronegative oxygen was interpreted in this way, and Stern and Volmer also cited as in agreement the relative retarding effects of He, N_2, and O_2 on the photo-decomposition of ozone in ultra-violet light. Kistiakowsky (*Z. physikal. Chem.*, **117,** 337, 1925) regarded the resonance potential of the added gas as a measure of the inelasticity of the collision concerned and thus of the extent of deactivation. He showed that a rough inverse parallelism exists between the retarding effects of He, A, N_2, CO, CO_2, and O_2 on the photo-decomposition of ozone in red light and the resonance potentials of these gases. Neither of these relations can be a general one, however, as the extent of deactivation depends on at least three factors, viz., the nature of both colliding particles and the frequency of the radiation absorbed by one of them.

In the example just quoted—the photochemical decomposition of ozone—the effects of different substances are found to be quite specific, but this is not always the case. An example is afforded by the non-specific retarding influences of electrolytes on the photo-decomposition in aqueous solution of potassium persulphate (see p. 489). Here it is possible that deactivation is essentially due to the fact that the retarding substances are electrolytes and that specific influences are masked by electrolytic dissociation, but it is not clear why the uni-univalent KOH should exert the same effect as the uni-bivalent electrolytes K_2SO_4 and H_2SO_4.

There are known a number of photochemical reactions in which degradation of energy of activation into heat does not occur to an appreciable extent, in spite of conditions apparently favourable for such dissipation of energy. Two possible explanations may be advanced: (1) the activated molecules are peculiarly stable with respect to collisions, and either a small fraction only of impacts causes degradation of energy or each collision results only in a small energy loss; (2) the reaction is one involving atoms or radicals which are formed in each elementary process of absorption. Recent work favours the latter view, though previously the paper of Stern and Volmer (*loc. cit.*) had caused theoretical speculation to incline towards the former. Thus, the photochemical decomposition of HI is associated with a quantum yield which is unaffected by high concentrations of nitrogen, and it is now universally regarded as an " atom " reaction. Also, the bromine-sensitised conversion of maleic ester into fumaric ester, in which the yield is uninfluenced by dilution with CCl_4 and for which Eggert at one time postulated an activated molecule theory, is now interpreted in terms of atoms and radicals. If, however, an activated molecule theory be adopted for a reaction in which little degradation of energy of activation into heat takes place, it is usually necessary to make the additional assumption that the activated molecules possess an exceptionally long life, considerably greater than 10^{-8} sec., the average life of a Bohr state. An example is the chlorine-sensitised decomposition of ozone (see Chapter XI.), in which the rate of reaction is independent of the concentration of ozone. Here, if activated Cl_2 molecules be regarded as the active agents in the change, one is forced to assume that their average life is greater than 10^{-7} sec.

More specialised explanations of low quantum yields than that of the general theory of deactivation by collision have been advanced for certain reactions. That suggested by Warburg for the reciprocal transformations of maleic and fumaric acids may be so regarded. In both reactions, the primary process was assumed to be a driving apart of two portions of the absorbing molecule, considerations of probability then determining whether the " excited " molecule reverts to the original or to the isomeric form. As the quantum yields of *both* processes are considerably less than unity, the theory involves either the assumption that the efficiency of either primary process is small (a view not taken by Warburg) or the hypothesis that, following either primary process, the probability of the two parts recombining to form the original molecule is much greater than the probability of formation of the isomer. The latter suggestion appears the more probable. A still more specialised theory is that of Weigert and Brodmann for the transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid (p. 493). Special assumptions are also necessary in the case of the chlorophyll-sensitised assimilation of carbon dioxide, a very endo-energetic reaction in which more than one quantum per molecule transformed is required. In this reaction it is improbable that two or more quanta are absorbed by the same absorbing molecule; it appears necessary to assume that comparatively stable intermediate products are formed, which also are photosensitive in the same spectral region as the sensitiser.

Another possible general explanation of low quantum yields has already been mentioned in connection with the effect of wave-length on quantum efficiency. All absorbing molecules may not be sufficiently activated to enable them to react, owing to molecules originally in the lower quantum states not receiving energy sufficient to raise them to the critical energy level.* Discussions of this aspect of photochemical change have been given by Tolman (*J. Amer. Chem. Soc.*, **45**, 2285, 1923) and Allmand (*Trans. Faraday Soc.*, **21**, 438, 1926), but no specific reactions have been cited as examples to which these ideas are applicable. It follows from their treatment that reactions which fall in this category should have—at low temperatures—small quantum yields which increase markedly on raising the temperature, i.e. these reactions should have high temperature coefficients. In order to discuss more fully this explanation of low quantum yield, we consider here the relation—predicted by the theory—between temperature coefficient and quantum yield when applied to a specific case. A "unimolecular" photochemical reaction which at ordinary temperatures has a temperature coefficient of 1·40 is interpreted by assuming that the photolyte before illumination consists of molecules in two different quantum states, with a difference of 6000 cal. per mole in their internal energy contents. Tolman shows that the relative numbers of molecules in the first and second quantum states are given by the expression

$$\frac{N_1}{N_2} = \frac{p_1 e^{-\epsilon_1/RT}}{p_2 e^{-\epsilon_2/RT}}.$$

Here ϵ_1 and ϵ_2 are the average energy contents (per mole) of the two quantum states; p_1 and p_2 are *a priori* probabilities of the two states, and their ratio may be taken without large error as not far removed from unity. Substituting this value, making $\epsilon_2 - \epsilon_1 = 6000$, and placing $T = 300$, one obtains $\frac{N_1}{N_2} = 22{,}000$. This means, of course, that practically all the molecules are in the lower quantum state. We are at present taking the view that molecules in both states absorb light of the given frequency, but that only those in the second state react. Before anything can be predicted about the deficiency in quantum yield, it is necessary to consider the relative absorption coefficients of the two states. Two cases may be differentiated, (α) when the absorption coefficient of the second quantum state is considerably greater than that of the first, and (β) when the two absorption coefficients are of the same order of magnitude or that of the second quantum state is the smaller. It is clear that if (β) applies to the example under consideration, the reaction will have an extremely small quantum yield, unless secondary reactions (" chain " processes) intervene. On the other hand, when the absorption coefficient of the reactive molecules is very great compared with that of the non-reactive variety, one may obtain quantum yields up to unity,* the limiting value for the case of non-absorption by molecules in the lower quantum state. It may be shown that in case (β) part of the increase in reaction velocity on raising the temperature will be due to increased absorption of radiant energy. Thus, to take an example, suppose the quantum efficiency of the process were 0·2 at room temperature, this means that molecules in the first quantum state absorb the fraction 0·8 of the absorbed energy. The fraction (x_1) of the energy absorbed by such molecules is given by

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* This is one of the two cases in which preliminary activation might increase the photochemical reaction rate. The other is when the molecules in the lower quantum states do not absorb light of the wave-length employed.

$$x_1 = \frac{i_1 c_1}{i_1 c_1 + i_2 c_2},$$

in which c_1 and c_2 are the concentrations of the two types of molecules and i_1 and i_2 their absorption coefficients. Placing $x_1 = 0{\cdot}8$ and $\frac{c_1}{c_2} = 22{,}000$, one obtains $\frac{i_2}{i_1} = 5500$. Suppose now the temperature is raised 20°, this involves an increase in the reaction rate in the ratio $(1{\cdot}4)^2 : 1$ or $2 : 1$ approximately. The ratio of the concentrations of molecules in the two states is then given by

$$\frac{N_1'}{N_2'} = \frac{c_1'}{c_2'} = 11{,}000.$$

Making the assumption that small changes in temperature do not markedly affect the absorption coefficients i_1 and i_2, one now obtains for the fraction (x_1') of energy absorbed by molecules in the lower quantum state

$$x_1' = \frac{i_1 c_1'}{i_1 c_1' + i_2 c_2'} = \frac{11000 i_1}{11000 i_1 + 5500 i_1} = \frac{2}{3}.$$

The non-reactive molecules now take only two-thirds of the absorbed energy, and the quantum efficiency is 0·33. Since from the value of the temperature coefficient one would have anticipated a quantum efficiency of 0·4, it follows that one-third of the increase in reaction rate caused by raising the temperature 20° is due to increase in the *total* absorption.

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* For simplicity, we postulate the simplest possible case, in which secondary processes do not magnify the quantum yield. The reaction might, for example, be an isomeric change $A_1 + h\nu \rightarrow A_2$.

We may summarise as follows. Practically all photochemical reactions whose quantum yields have been determined have values of γ greater than 0·01. The theory under consideration predicts still lower yields, unless the energy absorbed by molecules in the higher quantum state is an appreciable fraction of the total absorption. The theory then might be valid for actually measured cases, (*a*) when large preliminary activation is necessary (high temperature coefficient) in which event it is necessary that the absorption coefficient of molecules in the higher quantum state be very great, or (*b*) when smaller preliminary activation is required and an appreciable fraction of potentially reactive molecules is already present in the system. In either case, however, one would anticipate that the percentage increase in reaction velocity (using light of constant intensity) caused by increase of temperature would be greater than the corresponding increase in quantum efficiency. These conclusions might be expected to apply to photo-reactions in which the secondary processes are necessarily coupled in a simple stoichiometric manner with the primary process. As, however, this condition rarely applies—secondary processes as a rule exercising a predominating influence—one can anticipate that only feeble indications, if any, of the predicted relation between quantum efficiency and temperature coefficient will be obtainable. So far, there are insufficient data by means of which the relation may be tested, as practically no measurements of the effect of temperature on quantum yield have yet been carried out.

Another possible cause of low quantum yields in photochemical processes is deactivation by radiation, i.e. by emission of the absorbed energy as fluorescence or resonance radiation before chemical transformation occurs. Since, however, the life period of an excited molecular state is normally of the order of 10^{-8} sec. and since in gases at ordinary pressures the mean time between collisions is about 10^{-10} sec., it is clear that, before it spontaneously radiates the absorbed energy, the excited molecule has many chances of colliding and so effecting the energy adjustments leading to chemical reaction or to degradation of energy into heat. Normally, therefore, one would anticipate that for reactions in the liquid state and in gases at ordinary pressures, no loss of energy under this head occurs. For gas reactions at low pressures ($p < 1$ mm.) the case might be different; the few cases so far studied (decomposition of HI, decomposition of NH_3) do not, however, afford examples of this type of loss of energy since primary decomposition occurs as a result of absorption.

There is, however, one class of photo-reaction in which there may be considerable loss of energy by fluorescent emission, namely, the photo-processes entered into by organic dyestuffs (fluorescein, eosin, etc.) in liquid solution. Though these reactions, of which the oases investigated are usually oxidations by air or reactions between the fluorescent dye and polyalcohols (e.g. glycerine), are complex processes whose nature and mechanism have not been elucidated, they promise to be of importance, since the correlation of the chemical reaction with the fluorescence appears likely to furnish information regarding the properties of activated molecules and of deactivational processes. It has been shown by F. Perrin (cf. *Compt. rend.*, **184**, 1121, 1927) that in an illuminated solution of a fluorescent dye, the close proximity to an excited molecule of a molecule of the same species, or more generally of a molecule which absorbs in the same spectral region, increases the probability of the return of the activated molecule to the normal state *without emission of light.* Thus there results on increasing the concentration of the dyestuff a diminution in the fluorescent capacity of the solution and also of the mean life of the activated state. Closely connected with this "resonance induction" are the phenomena accompanying the photo-reactions of these dyes, in particular the photo-reaction between methylene blue and glycerine studied by J. Perrin and Choucroun (*Compt. rend.*, **183**, 329, 1926). They found that in this process the ratio $\frac{\text{velocity}}{\text{energy absorbed}}$ decreases very greatly on increasing the concentration of dye, a 250-fold increase in the concentration causing a 120-fold decrease in the velocity (per unit of light energy absorbed). This decrease in photochemical reaction rate with increasing concentration of photolyte, as also the decrease in the fluorescence, is a consequence of the increasing proximity of the dye molecules, with increase in the degradation of the absorbed energy into heat. (The chemical reaction taking place in this and analogous cases is probably the reduction of the dye to a leuco-derivative together with oxidation of the alcohol to an aldehyde or ketone.)

F. Perrin (*loc. cit.*) has also shown that an analogous action on the fluorescent capacity of dye solutions is caused by certain substances which possess no absorption bands near to those of the dye. Such are the easily oxidisable inorganic ions I', S'', and SCN' and also certain organic bodies such as phenols, aromatic amines, hydroquinone, uric acid, and phenylhydrazine. These substances (termed "antioxygens") diminish the fluorescence of dye solutions without reacting chemically with the dye, and, according to Perrin, exert a general non-selective deactivating action ("forced induction") on excited molecules. These "antioxygens" diminish the mean life of activated molecules in their vicinity and thus should exert a marked inhibiting action on the photo-reactions of fluorescent bodies, a conclusion experimentally confirmed by Privault (*Compt. rend.*, **184**, 1120, 1927).*

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* The fact that certain *thermal* reactions, notably auto-oxidations (cf. pp. 641-3), are strongly retarded by these "anti-oxygens" supports, according to F. Perrin, the chain theory of such reactions. A pure thermal reaction should not be inhibited by these substances, since the concentration of reactive molecules depends solely on the temperature, thermodynamic considerations showing that a catalyst cannot affect the concentration of active molecules. One must therefore seek for the origin of the energy of activation in these

Reactions with Quantum Yields Approximating to Unity.—These may perhaps be divided into two classes—(*a*) those in which γ is practically unity, and (*b*) those in which γ is a small whole number, usually two or three. Reactions in the latter category can usually be simply interpreted, as was done by Warburg for the photo-decomposition of HBr, by making legitimate assumptions regarding the secondary reactions which follow the primary "light" process. If the coupling of the primary and secondary processes is a rigid one, we thus arrive at a simple stoichiometric relation between the number of molecules reacting and the number of quanta absorbed. Such a relation exists for the photo-decompositions of HI and HBr, in which cases the quantum yield is two and is independent of the conditions of experiment (see however, p. 479). The same quantum yield is found for the photolysis in the gaseous state of Cl_2O, whether non-sensitised or sensitised by chlorine, but in this case a high temperature coefficient is associated with the process, which probably implies an increased quantum yield on raising the temperature. The lower quantum yield ($\gamma = 1$) in CCl_4 solution also remains unexplained. The chlorine-sensitised decomposition of ozone is another reaction with a quantum yield of two. Here, again, the whole number relation would appear to be fortuitous, since, according to Weigert (*Z. Elektrochem.*, **14,** 591, 1908), the reaction has a temperature coefficient of 1·2.

Reactions which can be classified under (*a*) are the photochemical bromination of hexahydrobenzene, the reaction between CCl_3Br and Cl_2, the bromine-sensitised oxidation of CCl_3Br, the reaction between ferrous ions and iodine, the decomposition of uranyl oxalate, and the hydrolysis of monochloracetic acid. The photochemical decompositions of AgCl and AgBr also have quantum yields of unity in their initial stages. It would seem, however, that most of these processes only obey the Einstein relation over a more or less limited range of experimental conditions and that outside this range considerable deviations may be expected.

The experimental result of a quantum yield approximating to unity is doubtless due in certain cases to the simultaneous operation of opposing factors which would separately tend to produce high and low yields respectively. Thus, if only a fraction of the light-activated molecules succeed in entering into reaction, but if those which do react start a "chain" involving further activation by reaction products, the two effects might approximately balance in certain cases. This is possibly what occurs in the photochemical decomposition of ozone in visible light. The quantum efficiency of this reaction under certain conditions of experiment is in the neighbourhood of unity. It is, however, dependent on the concentration of ozone, and is dimin-

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auto-oxidation processes in a source other than thermal molecular agitation, and one finds this in the energy liberated by the reaction itself. A "chain" process of the type postulated by Bodenstein and by Christiansen and Kramers must be presumed.

ished by oxygen and to a lesser extent by other gases. The action of these gases has been ascribed to deactivation of ozone molecules on collision. If this explanation is correct it follows from the experimentally determined values of the quantum yield that another factor tending to magnify the yield must also operate, and this is most probably re-activation by reaction products yielding a chain of short length. Similar considerations are probably applicable—among other reactions—to the photolysis of chlorplatinic acid. The quantum yield of this reaction is remarkably sensitive to variation in the wave-length of the activating light. For solutions of strength $10^{-4}N$, γ is 4·2 with $\lambda = 238\,\mu\mu$, but has fallen to 0·093 with $\lambda = 310\,\mu\mu$, while with $\lambda = 546\,\mu\mu$, γ has the very low value of 0·0038. It is probable that "chain" reactions are operative when short wave light is used, deactivation processes with long wave light; with light of intermediate frequencies, the two effects about balance yielding quantum efficiencies near unity.

Reactions with High Quantum Yields.—It is unnecessary at present to add to the discussion given above (pp. 447-462). Additional cases are dealt with in Chapters X. (H_2—Cl_2 reaction) and XII. (auto-oxidation processes).

Effect of Concentration of Photolyte, Light Intensity, Temperature, and other Factors on Quantum Yield.—As it is not possible briefly to summarise the manifold effects of concentration, temperature, solvent, etc. on quantum yield and as certain of them are reserved for treatment in Chapter XII., we shall at present draw attention only to a few points arising in this connection.

The effect of variation of the concentrations of the reacting substances has naturally been investigated in practically all experimental determinations of γ. Confining our attention to reactions in which the absorbing substance is a reactant, two classes of reactions give strikingly different results; in the one, the quantum yield increases strongly with increasing concentration of photolyte, in the other, marked diminution in γ attends increase in concentration of the absorbing reactant. In the former category are reactions with high values of γ ("chain" reactions), examples being the photo-decomposition of H_2O_2 and of O_3 and the combination of CO and Cl_2 and of H_2 and Cl_2. The variation in the quantum yield in the last of these reactions is specially marked, as seen by comparison of the experimental results of Kornfeld and Müller with those of Marshall. The former, employing stoichiometric mixtures of H_2 and Cl_2 at atmospheric pressure, found $\gamma = 10^5$; the latter, with mixtures containing an excess of H_2 but at a total pressure of 0·01 mm., obtained a quantum yield of 20. Evidently the length of the chain in this reaction is a function of the collision frequency.

The most marked cases of the reverse effect—diminution in γ with increasing concentration of photolyte—seem to be the photo-reactions of fluorescent dyes, such as the reaction between eosin or methylene blue and glycerol (p. 507). Here there appears to be a specially marked deactivating influence of normal dye molecules on the excited dye molecules.

An increase of γ with increasing concentration of photolyte is encountered in many reactions in aqueous solution (e.g. the photolysis of KNO_3 and of the chlorplatinic acids). A possible interpretation of the results in these cases is that the absorbing molecule can react only when it collides with non-activated molecules of the same kind, if it has not previously lost its excess energy by non-reactive collision. An exception is the photo-decomposition of oxalic acid in aqueous solution. In all these cases the effect of concentration is probably a composite one, comprising (*a*) a " field " effect on the process of absorption, and (*b*) an ionic catalytic effect on the secondary processes. Photochemical reactions of electrolytes have been discussed by Berger (*Rec. trav. chim.*, **40,** 153, 387, 1921 ; *ibid.*, **44,** 49, 1925), who has attempted to apply to them the theory of complete electrolytic dissociation of Debye and Hückel together with Bronsted's views (cf. *Z. physikal. Chem.*, **102,** 169, 1922) on ionic catalysis in thermal reactions.

It is to be anticipated that a dependence of γ on concentration is inherent in all photochemical processes, but that in certain reactions of the " primary decomposition type " it is not appreciable over wide ranges of concentration. Such cases are the decomposition of NH_3 and especially of HBr and HI. In the last of these cases, the quantum yield in the dilute gaseous state is the same as that in condensed liquid HI. In aqueous solution or in CCl_4, however,—the reaction apparently still being a primary decomposition—a dependence of γ on the concentration of HI is obtained.

The influence of light intensity on quantum yield has been but little subjected to systematic investigation, though the data on the kindred relation between light intensity and reaction velocity (cf. p. 407) supply for most reactions the necessary information. The general conclusion which at the present time is to be drawn is that in the great majority of photo-reactions the velocity of the primary process is proportional to the light intensity over wide variations of the latter, and that in many cases the same holds for the net process, i.e. γ is independent of I_0. In such processes as the decomposition of HI and HBr, for example, whose quantum yields are independent of wave-length and of concentration of photolyte, an effect of intensity on γ is not probable—at least not till exceedingly high intensities are reached. The exceptions so far encountered fall into two classes : (*a*) those reactions whose velocities are proportional to the square root of the intensity—and whose quantum yields therefore diminish with increasing intensity,—which cases are fully accounted for by the type of reaction mechanism assumed, and (*b*) those reactions of dyes (cf. p. 411) in which γ increases with increasing intensity. In the latter, a double activation and thus an influence of intensity on the primary " light " process *may* be effective, such, for instance, as has been detected in measurements of the fluorescence of mercury vapour (p. 149).

The influence of temperature on photochemical reaction velocity is of theoretical importance and it has been extensively studied, yet practically no direct measurements of the variation of quantum yield with temperature have been made. In nearly all cases, the temperature coefficients of photochemical reactions are based on comparisons of the velocities at different temperatures with *incident* light of constant intensity. If the variation of γ with temperature is required from these measurements, the assumption must be made that no appreciable change in the absorption of light occurs over the temperature range investigated. As a general rule, it is likely that no serious error is thereby introduced; since, however, the absorption bands of most substances are displaced by increase of temperature slightly in the direction of increasing wave-length, the possibility remains that in certain cases for which the light employed lies entirely on the long wave side of the band, an increase of temperature may cause an appreciable increase in absorbed energy. The observed temperature coefficient would in such cases be artificially raised. The reverse case of decreased absorption consequent on a rise of temperature is also possible.

CHAPTER X.

THE HYDROGEN-CHLORINE AND CARBON MONOXIDE-CHLORINE REACTIONS.

THE PHOTOCHEMICAL UNION OF HYDROGEN AND CHLORINE.

The most interesting and most studied of photochemical reactions is the union of hydrogen and chlorine in the light. The large amount of material published on this reaction has so far served mainly to reveal and emphasise its extreme complexity, and it is to be admitted that as yet there is no general accord with respect to many of the anomalous characteristics of the process. This disagreement exists in the experimental results of different investigations, and is particularly marked in the theoretical interpretation of such data as are generally accepted. However, the evolution of photochemistry is intimately associated with the history of this reaction; it was the first photochemical process to be subjected to quantitative study, and many new and interesting developments have been initiated or advanced as a result of work on the photo-combination of hydrogen and chlorine. As a result of these developments and with new methods of attack, the immediate centre of interest has changed from time to time. In the older work, attention was chiefly focussed on the phenomena associated with the initial stages of the process, in particular with " the overcoming of the reaction resistance " ; at the present time, the more immediate concern of the investigator is the study of the reaction kinetics and the development therefrom of a satisfactory " mechanism " for the process. In what follows, we propose to deal only very cursorily with the earlier work ; bibliographies and more complete summaries of this will be found in Mellor's *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II., pp. 148-157 (Longmans, London, 1922), and in Weigert's *Die Chemischen Wirkungen des Lichts* (*Ahrens Sammlung*, **17,** pp. 183-296, 1912).

Photochemical Induction.—The appearance of an induction period in chemical processes is not peculiar to the hydrogen-chlorine reaction, though this forms one of the first and most studied examples. Induction periods are also encountered in other photochemical reactions of chlorine—for example the reactions with carbon monoxide, with propane, and with acetylene. They are also observed in such thermal processes as the Landolt reaction (the reaction between iodic and sulphurous acids), the solution of metals in acids, the reaction between potassium permanganate and oxalic acid, and many others (cf. Mellor, *Chemical Statics and Dynamics*, Longmans, London, 1904). In such cases it is generally recognised that the period of induction may be due to one of the three following causes :—

(*a*) The reaction occurs in stages, a consequence of which is—under certain conditions—that the velocity increases with time.
(*b*) Autocatalysis, or the formation of a positive catalyst as the reaction progresses.
(*c*) The destruction of an inhibitor or negative catalyst initially present.

The induction period in the hydrogen-chlorine reaction may be of a very well-marked type, and for some time following Bunsen and Roscoe's work much attention was paid to this initial reaction stage, then regarded as of fundamental importance but now shown to be of but incidental significance. The later work has conclusively established the general causes underlying the induction period, and has shown that such a reaction stage is not necessarily a precursor of photochemical change in this reaction. Certain features of the process have, however, not yet been satisfactorily accounted for, in particular the nature and mechanism of the reactions which occur during the induction.

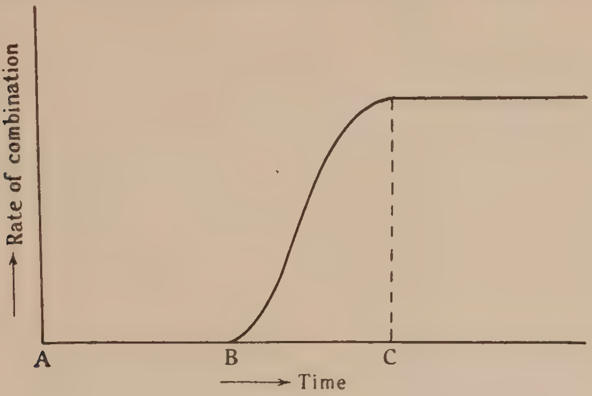

FIG. 46.

Bunsen and Roscoe established the general characteristics of the induction period. The usual type of reaction course obtained by them with their actinometer is shown in Fig. 46, in which the rate of combination, as measured by the rate of motion of actinometric liquid along the scale, is plotted against time of insolation. They found that the period of inertness (AB in the diagram) and also the period of induction (AC) may vary greatly according to the conditions. Other things being the same, the induction period increases with increasing depth of illuminated gas column, and is decreased by increasing the light intensity. A once "induced" gas mixture, after cutting off the illumination, returns to the inactive state (*photochemical deduction*). The period of induction on re-illumination is, however, shorter than the first. Finally, Bunsen and Roscoe denied Draper's observation that separate illumination of the chlorine diminished the induction period; they found rather that only the *mixture* of hydrogen and chlorine could be induced. Bevan (*Phil. Trans.*, **202**A, 71, 1903) showed, however, that Bunsen and Roscoe's inability to confirm the Draper result was due to their having passed the pre-illuminated chlorine gas through water before testing its activity with hydrogen, in which process the acquired gain in reactivity was lost. The observation of Draper has also been confirmed by Wendt, Landauer, and Ewing (*J. Amer. Chem. Soc.*, **44,** 2377, 1922). Bunsen and Roscoe also inferred from their work that addition of oxygen to a hydrogen-chlorine mixture—which as previously stated markedly diminishes the maximum speed of reaction—also diminishes the time necessary for the attainment of the limiting maximum rate. Burgess and Chapman (*J.C.S.*, **89,** 1399, 1906) showed, however, that oxygen has practically no effect on the period of induction.

Bunsen and Roscoe themselves regarded the induction period as the time required for the light to overcome the resistance of some force opposed to that of chemical affinity, while others such as Bevan (*loc. cit.*), Pringsheim (*Wied. Ann.*, **32,** 384, 1887), and Mellor (*J.C.S.*, **81,** 1292, 1902) adopted various forms of the intermediate-compound theory ((*a*) above). Pringsheim assumed the intermediate production of Cl_2O, the scheme represented by

$$\begin{gathered} Cl_2 + H_2O \rightarrow Cl_2O + H_2 \\ Cl_2O + 2H_2 \rightarrow 2HCl + H_2O \end{gathered}$$

being suggested. This was disproved by Mellor (*loc. cit.*) who showed that neither hypochlorous acid nor its anhydride shortened the period of induction. In place of the latter substance, Mellor assumed as intermediate compound a complex of the type

$$xCl_2 \,.\, yH_2O \,.\, zH_2$$

and Bevan also postulated the formation of aggregates of such a type or of Cl_2—H_2O complexes. Though these theories are not now of importance in relation to the induction period, they are still of significance in respect of the rôle played by water in the reaction and are mentioned later in this connection (cf. pp. 537, 564 *et seq.*).

Our present views on the induction and associated phenomena in the hydrogen-chlorine reaction we owe mainly to the classical work of Burgess and Chapman (*loc. cit.*). They showed conclusively that the induction period is due to impurities which are destroyed by chemical reaction in the initial stages of the process. This standpoint appears to have been originally taken by van't Hoff, who rejected the view that the induction period is inherent in the change itself, and who regarded it rather as a sign that some essential precaution in the experiment had been neglected. As a result of exhaustive tests, Burgess and Chapman showed that the phenomenon of induction is due to traces of impurity normally present in chlorine gas or in the actinometer liquid, and that the inhibitor may be destroyed by chlorine either photochemically or by heating for some time at 100°, with consequent shortening of the induction period. They were led to suspect that ammonia is the cause of the inhibition, and this was confirmed by the results of experiments in which traces of this substance were added to the previously "activated" actinometric liquid or chlorine. They found that the deactivating effect of ammonia, as measured by the period of induction, is very marked and is roughly proportional to the amount added. Solutions rendered "inactive" by addition of ammonia could be activated again by heating to 100° in the presence of chlorine; in fact, all the properties of naturally "inactive" chlorine or actinometric liquid could be artificially reproduced by the contamination of the active chlorine or liquid by ammonia. Burgess and Chapman further found that not only ammonia but also organic nitrogeneous substances which decompose into ammonia—for example, egg albumen—similarly bring about the induction effects. The action of ammonia, however, does not lie solely in its capacity to react with chlorine, as other substances which also react with chlorine, such as alcohol, benzene, and sulphur dioxide, do not bring about an induction period in a system free from ammoniacal impurities. Addition of such oxidising agents as aqua regia, HNO_3, $KMnO_4$, and H_2O_2 is also unaccompanied by induction effects. The "deduction" observed by Bunsen and Roscoe and others is explained by Burgess and Chapman as follows. By illumination of H_2—Cl_2 mixtures in the glass actinometer, the induction period normally ends with the establishing of a stationary state, when the rate of destruction of the inhibiting impurities balances their rate of supply from the glass walls or from the taps or from the actinometer liquid. The rate of supply may be conditioned either by diffusion of the actual inhibitor or by the rate of formation of this inhibitor by destruction of organic material. When the illumination is withdrawn, the concentration of inhibitor gradually increases, so that on re-illumination a further period of induction is necessary before the re-attainment of the maximum velocity. It is possible, however, to remove the deduction period completely if leaks into the apparatus are eliminated and precautions are taken to remove completely from the actinometer and actinometer liquid all organic material. Burgess and Chapman constructed from quartz, whose surface adsorptive capacity is small, an actinometer in which no deduction effects whatsoever were obtained. After a small initial period of induction, no further inhibitions of the reaction were found; even after a week, the indicator liquid responded immediately and with maximum velocity to illumination. Similar success in elimating deduction is also attainable but with somewhat more difficulty in an all-glass apparatus.

The actual inhibiting substance formed from ammonia or nitrogeneous organic bodies is taken to be a chlorine derivative of ammonia, probably NCl_3 or a chloramine NH_2Cl or $NHCl_2$. This, though probably the most powerful,* is not the only inhibitor for the hydrogen-chlorine reaction. The inhibiting effect of oxygen, which is much less, had already been noted by Bunsen and Roscoe. Chapman and MacMahon (*J.C.S.*, **95**, 959, 1909) examined the retarding effect of oxygen quantitatively and found that the sensitivity (i.e. the maximum constant rate) is inversely proportional to the oxygen content. Inhibition by O_2 is, however, *not* characterised by an induction period; a hydrogen-chlorine mixture containing O_2 but free from other inhibitors reacts *immediately* at its maximum speed on illumination. The nature of the difference between the inhibiting actions of O_2 and of NCl_3 will be reverted to later. Further work by Chapman and MacMahon (*J.C.S.*, **95**, 1717, 1909; *ibid.*, **97**, 845, 1910) showed that NO, which under the conditions of the experiment is converted into NO_2 and perhaps into NOCl, is also an inhibitor, though not so powerful a one as NCl_3. Ozone and chlorine dioxide also act in the same way, marked induction periods being found in each case; on the other hand, nitrous oxide and chlorine monoxide have no effect on the initial reaction rate.

The work of Chapman and his co-workers has thus established that inhibition of the photochemical union of hydrogen and chlorine is due to the presence of small quantities of one or more easily reducible substances, and that these inhibitors (excepting oxygen) are destroyed during the period of induction. Two remaining problems are:

(1) the nature of the processes by which the retarding agents are destroyed, and
(2) the mechanism of inhibition.

With regard to the first question, Chapman and MacMahon suggested that the destruction of the inhibitors NCl_3 and O_3 is due respectively to the photo-processes

$$(A)\quad NCl_3 + 3HCl \rightarrow NH_3 + 3Cl_2,$$
$$(B)\quad 3O_3 + 2HCl \rightarrow 4O_2 + H_2O + Cl_2.$$

As an alternative they advanced the view that the inhibitor is destroyed by a chlorine-sensitised reduction with H_2. These are not the only possibilities; a more complete but not exhaustive list of possibilities is as follows:—

(I) Reduction of the inhibitor:
  (*a*) by a chlorine-sensitised process with HCl or with H_2;
  (*b*) by direct photochemical action with HCl or with H_2;
  (*c*) by activated HCl molecules.

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* Chapman (*Science Progress*, **25**, 72, 1912) estimates that the sensitivity of an H_2—Cl_2 mixture is reduced at least 100-fold by the presence of 1 molecule of NCl_3 in 10^6 molecules of $(H_2 + Cl_2)$.

(II) Destruction of the inhibitor:
  (*a*) by direct photochemical action;
  (*b*) by a chlorine-sensitised reaction.

Naturally, not all these possibilities may be entertained for certain inhibitors. In the case of oxygen, for example, processes (II) (*a*) and (II) (*b*) are obviously inoperative, as also is (I) (*b*) in visible or long wave ultra-violet light. The small fraction of the inhibiting oxygen which disappears in an experiment must then be attributed either to I (*c*) or to one of the two processes under I (*a*). The most probable would appear to be the chlorine-sensitised combination of hydrogen and oxygen.* With nitrogen trichloride as inhibitor, the processes II (*a*) and/or II (*b*) cannot be left out of account since (α) NCl_3 is decomposed by blue light (Bowen, *J.C.S.*, **123,** 1199, 1923), and (β) by illumination—before mixing with hydrogen—of chlorine containing an inhibiting impurity, presumed to be NCl_3, the subsequent induction period on insolation in the presence of hydrogen is diminished.

Doubt thus exists in respect of the reaction by which the inhibitor is destroyed; still more doubtful is the mechanism of inhibiting action. This may or may not be bound up with the method of destruction of the inhibitor. In either case, it is of course necessary that the inhibitor must very markedly reduce the length of the "chain" in hydrogen-chlorine combination. For example, if we take the view that the mechanisms of inhibiting action and of destruction of the inhibitor are one and the same, and for the latter postulate reaction with HCl, e.g. by (*A*) or (*B*), the rate of formation and consequent equal rate of destruction of HCl during the period of total inhibition must be very much less than the rate of HCl formation in a mixture free from the inhibitor (either O_3 or NCl_3). In modern parlance, the action of the inhibitor would in such a case be to react with activated hydrochloric acid molecules and break the "chain." An example of a possible mechanism of inhibition quite distinct from the reactions which result in the destruction of the retarder is that suggested by Nernst for the action of oxygen. It is postulated that the stationary concentrations of the carriers of the chain, H and Cl atoms, are diminished by reaction with O_2, thus—

$$H + O_2 \rightarrow HO_2$$
$$Cl + O_2 \rightarrow ClO_2.$$

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* The two remaining possibilities are both represented by the equation

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O,$$

in the one case, however, a chlorine-sensitised reaction, in the other a reaction between activated HCl molecules and O_2.

The photo-reaction between HCl and O_2 has been investigated by Richardson (*J.C.S.*, **81,** 801, 1887) who found that in sunlight reaction occurred only when liquid water was present, by Thiele (*Ber.*, **40,** 4914, 1907) and Coehn and Wassiljewa (*ibid.*, **42,** 3183, 1909) who observed reaction in dry gas mixtures using ultra-violet light, and by Weigert (*Ann. Physik*, **24,** 243, 1907) who found that the photo-process takes place only if chlorine is present, i.e. the reaction is a chlorine-sensitised one.

These reactions do not diminish the concentration of oxygen, however, since this gas is assumed to be continually re-formed by the processes

$$\begin{gathered} ClO_2 + Cl \rightarrow Cl_2 + O_2 \\ ClO_2 + H \rightarrow HCl + O_2 \\ HO_2 + Cl \rightarrow HCl + O_2 \\ HO_2 + H \rightarrow H_2 + O_2. \end{gathered}$$

The retardation by oxygen is here taken to be quite separate from the unspecified process by which oxygen is destroyed.

We have given above two possible mechanisms for inhibition; these, however, represent only a fraction of the numerous possibilities. It will be clear that each of the many "chain" mechanisms which have been postulated for H_2—Cl_2 combination, with their different unstable intermediate products or carriers of the chain, may involve one or more possibilities for the mechanism of inhibition. The only inhibitor whose action has been quantitatively studied * and for which definite reaction schemes have been postulated, and to some extent tested, is oxygen. It will be convenient to postpone further discussion of the retarding influence of this gas to a later section of this Chapter. Attention has previously been drawn to the marked differences between the retarding effects of O_2 and of NH_3 (NCl_3), and it appears somewhat doubtful whether a theory which satisfactorily accounts for the action of the one can be applicable to that of the other.

In view of the extremely high inhibiting power of NCl_3, the question arises as to whether it is at all possible to account for it on the basis of collisions between NCl_3 molecules and some "active" intermediate product of the hydrogen-chlorine reaction. According to Chapman this is the case. He calculates, on the assumption that a molecule of an active substance is always destroyed when it collides with a molecule of nitrogen trichloride, that the observed inhibiting effect of the latter is consistent with a mean life of $\frac{1}{40}$ sec. for the chain of active substances in a sensitive gas mixture containing no nitrogen trichloride. Weigert and Kellermann obtained experimentally for this period a value between $\frac{1}{20}$ and $\frac{1}{100}$ sec.

On the other hand, Norrish (*J.C.S.*, **127,** 2316, 1925) believes that the inhibiting effect of ammonia (or NCl_3) cannot be interpreted in terms of a homogeneous gas reaction. He accepts Chapman and MacMahon's mechanism of inhibition by oxygen and nitrogen peroxide (i.e. a chlorine-sensitised reduction of the inhibitor by hydrogen), but rejects it for the much greater inhibition by NCl_3. He points out that Chapman's original scheme for the *removal* of nitrogen trichloride, viz. $NCl_3 + 3HCl \rightarrow NH_3 + 3Cl_2$, is unsatisfactory, since NCl_3 would be continually re-formed and there would be no limit to the period of induction.

Norrish investigated quantitatively the phenomenon of the induction caused by ammonia in a glass apparatus containing no water, and in which the end of the induction period was indicated by the Draper effect registered as an increase of pressure by a glass Bourdon gauge. The nature of the results of one of his experiments is illustrated in Fig. 47. From the results of such experiments, in which known quantities of ammonia were added to reaction mixtures of known composition, Norrish found that the induction period T (measured by the period of inertness AB) is given by an equation of the type

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* See, however, Norrish's work (below) on inhibition by ammonia.

$$T = \frac{apv}{S}\left(1 - \frac{b}{P}\right),$$

in which p and P are the partial pressures of NH_3 and Cl_2 respectively, v and S are the volume of the reaction vessel and the illuminated surface area, and a and b are constants. Norrish explains these results on the basis of a theory that the primary photochemical process requires water as a catalyst and takes place only at the illuminated walls of the reaction vessel. The reaction centres thus started at the surface may then move outwards into the gaseous phase. With ammonia present, this gas is assumed to combine preferentially with the moisture film on the glass surface and thus to act as a poison to the ordinary photochemical action. The induction period lasts so long as there is sufficient ammonia present in the system to cover the surface. The removal of the ammonia, according to Norrish, occurs by the reactions

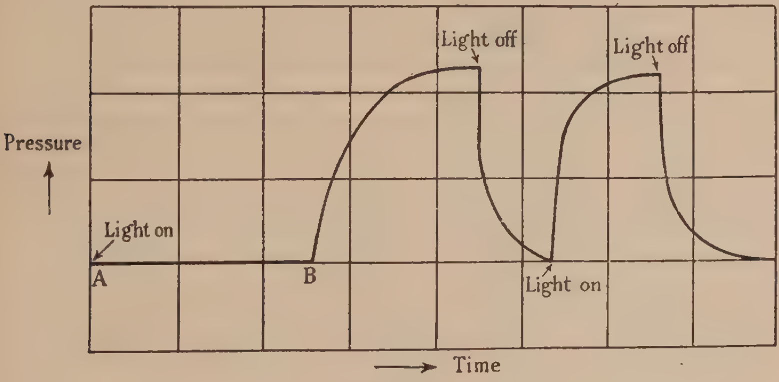

FIG. 47.

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$
$$6HCl + 6NH_3 \rightarrow 6NH_4Cl.$$

The fundamental basis of Norrish's theory, however, has been experimentally refuted by Coehn and Heymer (*Ber.*, **59,** 1794, 1926), who showed conclusively that the initiation of the photo-combination of H_2 and Cl_2 does not require the presence of a solid (or liquid) surface.

In one of their experiments a jet of H_2—Cl_2 gas issued from a narrow capillary into the atmosphere, and a narrow beam of light was concentrated on a portion of the jet well clear of any glass surface. The jet was directed into a U-tube immersed in liquid air, and analysis of the condensed products showed that considerable formation of HCl had taken place, in spite of the fact that the photochemical reaction occurred in presence of inhibiting atmospheric oxygen. It appears inevitable, then, that the inhibiting action of ammonia (or NCl_3) must also take place in the gaseous phase. The possibility remains, however, that the inhibiting action is distinct from the gradual destruction of the inhibitor which occurs during the induction period, and that this destruction may possibly be a photo-process occurring on the glass walls, as indicated by the general nature of Norrish's results. On the other hand, nearly all the latter's experimental data can almost equally well be accounted for on the assumption that the destruction of the inhibitor is a chlorine-sensitised reaction of zero order with respect to NH_3 (cf. ozone decomposition in presence of Cl_2 (p. 601)).

Photochemical Induction and Cloud Formation. — Bevan (*Proc. Roy. Soc.*, **72**A, 5, 1903) found, in experiments with the well-known C. T. R. Wilson apparatus, that cloud formation takes place in damp chlorine more readily (i.e. as a result of a smaller expansion) when the gas is illuminated than in non-insolated gas. He advanced the view that the union of hydrogen and chlorine involves the formation of condensation nuclei as the primary light process. Burgess and Chapman (*loc. cit.*) carried out experiments to determine whether the same impurities which are known to inhibit photochemical union of H_2 and Cl_2 exert a similar action on the readiness of cloud formation in electrolytic gas. They found that strong light is essential in the case of Cl_2 for the effect observed by Bevan, and that ammonia had no influence on the phenomenon. In sensitive H_2—Cl_2 mixtures, the Bevan effect is also found using light of moderate intensity; on the other hand, if NH_3 is present, the same expansion ratio for cloud formation is required as in non-insolated H_2—Cl_2 mixtures free from ammonia. Burgess and Chapman therefore concluded that the increased facility of cloud formation exhibited by illuminated chlorine itself can be of no significance for the photochemical reaction which occurs when H_2 is also present.

Reaction Kinetics.—The kinetic behaviour of hydrogen-chlorine systems under illumination is exceedingly complex. The experimental study of the relations which govern the velocity of the process has been confined almost exclusively to the laboratories of Chapman and of Bodenstein; but in spite of the valuable work carried out by both schools during the past fifteen years, general agreement has not yet been reached in regard to certain of the experimental facts themselves, and, corresponding to this lack of agreement, widely different views regarding the mechanism of the photochemical process have been upheld. It should first be noted that, up to the present, it has not been possible to prepare mixtures of H_2 and Cl_2 which are completely free from oxygen, so that in all cases the photochemical system dealt with is really a H_2—Cl_2—O_2 system. Since traces of oxygen exert an appreciable inhibiting effect on the combination of hydrogen and chlorine, it is not unlikely that the above-mentioned lack of agreement in the results of different workers may be traceable in part to small variations in the oxygen content of reaction mixtures.

The experimental techniques adopted by the two schools for following the course of reaction differ in general principle. Chapman and his co-workers have, in general, used a glass reaction vessel which is a modification of the Bunsen-Roscoe actinometer. Water or an aqueous solution being present to absorb the hydrochloric acid as it is formed, the pressure of the reacting gas mixture remains constant during illumination, and the extent of reaction at any instant is given by the diminution in volume of the gaseous phase. On the other hand, in Bodenstein's method the reaction vessel is of quartz, water is excluded from the system, and the reaction is allowed to proceed at constant volume. The composition of the reaction mixture at any time is then determined by freezing out the chlorine and hydrochloric acid and measuring the pressure of residual hydrogen at the temperature of liquid air by means of a quartz spiral manometer.

The actinometer method is the more convenient in operation, but certain disadvantages may be urged against its use for kinetic observations. In the first place, the presence of water in the reaction vessel—apart from its possible featuring in the reaction kinetics and the introduction thereby of unnecessary complications—may involve simultaneously the presence of inhibitors which would adversely effect the course of reaction. Again, working with the constant pressure actinometer, at least two separate experiments are necessary to test the effect of variation in the concentration of each reactant on the rate of reaction. Here, also, the presence of inhibitors in different amounts in the separate experiments may lead to erroneous conclusions. Chapman and co-workers have later used a modification of the actinometric method, whereby, although the hydrochloric acid is still absorbed in water, the volume of the reaction mixture is artificially maintained constant and the course of reaction followed manometrically.

We proceed to discuss the dependence of the rate of the photocombination of H_2 and Cl_2 on the variables light intensity, concentrations of reactants, and concentration of inhibiting oxygen. As previously mentioned, the latter substance is always present, but it is to be understood that the experimental data upon which the following conclusions are based refer to H_2—Cl_2—O_2 systems which exhibit no induction effects, i.e. from which all *destructible* inhibitors have been eliminated.

Dependence of Reaction Rate on Light Intensity. — The nature of this dependence sometimes affords a clue to the primary process which accompanies the light absorption. In certain photochemical reactions already mentioned which involve a halogen as the light-sensitive reactant, the fact that the rate of reaction is proportional to the square root of the light intensity is interpreted in terms of a primary dissociation of the halogen into atoms. Failure to obtain this dependence, however, does not necessarily eliminate the possibility of such a primary dissociation.

Draper and Bunsen and Roscoe, with the limited technique at their disposal, found that the rate of combination of hydrogen and chlorine—after the destruction of inhibitors—is directly proportional to the intensity of the light used. Baly and Barker (*J.C.S.*, **119,** 653, 1921), however, have stated that with increasing light intensity the maximum reaction velocity increases more than proportionately. Thus the rate of reaction was found to be increased ten times by a six-fold increase in the intensity. Cathala (*Compt. rend.*, **181,** 33, 1925) interprets the data of Baly and Barker as indicating proportionality between rate of reaction and $I_0^{3/2}$. Other workers, however, have failed to confirm this result. Kornfeld and Müller (*Z. physikal. Chem.*, **117,** 242, 1925) have verified the direct proportionality law over a sixty-fold range of intensity for reacting systems at atmospheric pressure, and Marshall (*J. Physical Chem.*, **29,** 1453, 1925) has found the same to hold true for a total pressure of the reacting system of about 6 cm. Hg. It should be mentioned that Kornfeld and Müller used the Bodenstein-Dux method of following the reaction, and Marshall employed a dynamic modification of the same. In both cases the oxygen content of the reaction mixtures must have been very low, since very high quantum yields were obtained. M. C. C. Chapman (*J.C.S.*, **125,** 1521, 1924) has carried out similar tests over a six-fold range of intensity using the actinometer method, and has found that the rate of combination of hydrogen and chlorine increases slightly less rapidly than the intensity. Previous kinetic data of the same worker have been interpreted by Berthoud (*Helv. Chim. Acta*, **7,** 324, 1924) as implying proportionality between rate of reaction and the square root of the intensity. Berthoud's arguments, however, have been adversely criticised by Thon (*Fortsch. der Chemie, Physik und physikal. Chemie*, **18,** Heft 11, 1926). D. L. Chapman (*Trans. Faraday Soc.*, **21,** 547, 1925) suggests that it is possible that " chlorine and hydrogen from which O_2 has been completely removed might combine at a rate proportional to the square root of the intensity of the light, or at least at a rate which could definitely be stated to be proportional to a power of the intensity lying between a half and one." While this may be so, it may be taken as definitely established that for such reaction mixtures as have so far been experimentally realised, the rate of the photochemical union is almost directly proportional to the intensity of the light.

Dependence of Reaction Rate on the Concentrations of Hydrogen and Chlorine.—The very marked diminution of velocity which Bunsen and Roscoe originally reported to be brought about by the addition of hydrogen to stoichiometric mixtures of hydrogen and chlorine has not subsequently been confirmed. It is probable that some oxygen, which inhibits the reaction, was introduced simultaneously with the excess hydrogen. Chapman and Underhill (*J.C.S.*, **103,** 496, 1913) were the first to examine in detail the rôle of hydrogen in the reaction kinetics. They found that with constant concentration of chlorine and with increasing concentration of hydrogen the rate of reaction is at first proportional to the latter concentration, but that a maximum velocity is obtained for mixtures containing about 30 per cent. of hydrogen. For higher concentrations of hydrogen, the rate of reaction fell off slowly from this maximum value, in other words addition of hydrogen appeared to have a slight, but distinct, inhibiting effect for concentrations greater than 30 per cent. A more complete examination of the kinetics of the reaction was carried out practically simultaneously by Bodenstein and Dux (*Z. physikal. Chem.*, **85,** 297, 1913). These authors found that the combination of *stoichiometric mixtures* of hydrogen and chlorine followed a second order course. Experiments with different partial pressures of hydrogen and chlorine showed, however, that the reaction was not a simple mass action. The rate of combination of the gases was determined only by the square of the chlorine concentration and was independent of the concentration of HCl and of the hydrogen content, provided this did not fall below one-quarter of the chlorine content. For lower concentrations of hydrogen, however, the rate of reaction was found to depend also upon the hydrogen content of the mixture. Bodenstein and Dux expressed their results by the empirical equation

$$\frac{dx}{dt} = k\frac{[Cl_2]^2[H_2]}{m + [H_2]} \quad . \quad . \quad . \quad . \quad (1)$$

in which $\frac{dx}{dt}$ is the rate of reaction as measured by the rate of disappearance of hydrogen, and k and m are constants. The value of the latter is such that it becomes negligible compared with $[H_2]$ when this is large. This relation and the results upon which it is based agree with Chapman and Underhill's observations in so far as the rate of reaction (for constant chlorine content) becomes proportional to the concentration of hydrogen at sufficiently low values of this concentration. It fails, however, to bear out their observation of the retarding effect of hydrogen at high partial pressures.

The Bodenstein-Dux formula fails also to take account of the experimental results of Chapman and Whiston (*J.C.S.*, **115,** 1264, 1919). These authors found that the rate of combination of H_2 and Cl_2 in stoichiometric mixtures of the two gases (containing also about 1·3 per cent. by volume of oxygen) is nearly independent of the total pressure. According to the Bodenstein-Dux relation, however, halving the pressure of such equimolecular mixtures should halve the sensitivity.*

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* Halving the pressure halves the chlorine concentration, and the velocity should thus be reduced to a quarter of its initial value. However, the *oxygen* concentration is also halved, and as shown later (p. 526) the velocity of photo-

Chapman and Whiston's result was later confirmed by M. C. C. Chapman (*J.C.S.*, **123**, 3062, 1923) in the course of an investigation involving extensive measurements with large variations of the concentrations of both chlorine and hydrogen. As a result of this work, she suggested the empirical equation

$$\frac{dx}{dt} = \frac{k_1[H_2][Cl_2]^2}{a[H_2]^{2-y} + [Cl_2]} \quad . \quad . \quad . \quad (2)$$

for the velocity of the process in so far as it is determined by the concentrations of hydrogen and chlorine. In this equation k_1 is a constant, the index y is a $+^{ve}$ constant less than one-half, and a is a factor dependent on the constant oxygen concentration in any one run. For reasonably small oxygen concentrations, the value of a is such that the first term in the denominator is negligible for low concentrations of H_2, the second term for high concentrations of this gas. This being so, the equation takes account of the following observations of M. C. C. Chapman.

(1) Low $[H_2]$:—

(*a*) for const. $[H_2]$, $\frac{dx}{dt} \propto [Cl_2]$;

(*b*) for const. high $[Cl_2]$, $\frac{dx}{dt} \rightarrow \propto [H_2]$.

(2) Intermediate concentrations of H_2 and Cl_2—approximately equimolecular mixtures:—

$$\frac{dx}{dt} \propto [Cl_2]^u[H_2]^{-v},$$

where $u \approx 1{\cdot}6 - 1{\cdot}7$ and $v \approx 0{\cdot}45$.

In this region of concentrations the order of the reaction is $u - v$, which is nearly unity. This result is in agreement with the observations of Chapman and Whiston already mentioned.

(3) High $[H_2]$ and low $[Cl_2]$:—

(*a*) for const. $[H_2]$, $\frac{dx}{dt} \propto [Cl_2]^2$;

(*b*) for const. $[Cl_2]$, $\frac{dx}{dt} \propto [H_2]^{-(1-y)}$,

in which y is a fraction less than $\frac{1}{2}$.

Thon (*loc. cit.*) has attempted to reconcile the discrepant observations of Bodenstein and Dux and of Chapman and co-workers in the following way. He assumes that one of Chapman's observations, viz. the retarding effect of excess of hydrogen, is in error and is possibly due to the unsuspected presence of oxygen in the hydrogen used. Using

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combination of H_2 and Cl_2 is inversely proportional to the oxygen pressure. The net effect of halving the total pressure should thus be, according to Bodenstein and Dux, to reduce the sensitivity to half of the initial value.

the Bodenstein-Dux technique, Thon has re-investigated the effect of hydrogen concentration on the rate of reaction (*Z. physikal. Chem.*, **124,** 327, 1926). With large excess of hydrogen, the rate of photo-combination of hydrogen and chlorine is found to be independent of the H_2 concentration and to be given by

$$\frac{dx}{dt} = k[\mathrm{Cl_2}]^2.$$

This agrees with the limiting case of Bodenstein and Dux's equation (1), but not of Chapman's equation (2) unless the index $(2 - y)$ in the denominator is unity. If Chapman's retarding effect of hydrogen be ignored, however, the remainder of her results are capable of expression by an equation of the form

$$\frac{dx}{dt} = \frac{k[\mathrm{Cl_2}]^2[\mathrm{H_2}]}{[\mathrm{H_2}] + n[\mathrm{Cl_2}]} \quad . \quad . \quad . \quad . \quad (3)$$

Thon now points out that a relation of this same type is equally applicable to the results of Bodenstein and Dux. The failure of the latter authors to appreciate the dependence of the "constant" m of their equation (1) on the chlorine concentration is attributable to the small value of the constant n in equation (3), which Thon finds to be only about 0·1. This being so, the term $n[\mathrm{Cl_2}]$ in the denominator assumes major importance only in the region of low concentrations of hydrogen and high concentrations of chlorine, and under these conditions the concentration of chlorine and therefore the term $n[\mathrm{Cl_2}]$ does not change greatly throughout the whole course of a run. On the other hand, in the region of stoichiometric mixtures the ratio $[\mathrm{Cl_2}]/[\mathrm{H_2}]$ does not alter much during the reaction, and therefore the degree of constancy of k throughout any one experiment depends very little on the value adopted for n. This is easily seen when k is expressed in the form

$$k = \frac{\frac{dx}{dt}}{[\mathrm{Cl_2}]^2}\left\{1 + n\frac{[\mathrm{Cl_2}]}{[\mathrm{H_2}]}\right\}.$$

It is not necessary, then, that the term $n[\mathrm{Cl_2}]$ should be altogether negligible compared with $[\mathrm{H_2}]$ in this region in order that the Bodenstein-Dux result $\frac{dx}{dt} \propto [\mathrm{Cl_2}]^2$ may hold true. This fact clears up one of the discrepancies between the work of Bodenstein and Dux and that of M. C. C. Chapman. The latter found, from two experiments with the same concentration of hydrogen and different concentrations of chlorine in the stoichiometric region, that the order of reaction with respect to the chlorine is 1·7. From the above equations it is clear that this may well be so provided $n[\mathrm{Cl_2}]$ is not negligible compared with $[\mathrm{H_2}]$, while at the same time the rate of reaction in each experiment would still conform approximately to the bimolecular law. As an alternative explanation of the apparent anomaly, Thon suggested (*Fortsch. der Physik, Chemie und physikal. Chemie*, **18,** Heft 11, 1926) that the values of the coefficient n might reasonably be very different under the different experimental conditions of Bodenstein and Dux on the one hand and of Chapman on the other.

From the above considerations, we may therefore take an equation of the form of (3) to represent the kinetic course of the photochemical reaction, in so far as it is determined by the concentrations of hydrogen and chlorine. It might be mentioned that the recent experimental data of Cremer (*Z. physikal. Chem.*, **128,** 285, 1927), who has investigated the reaction in a different connection, are also consistent with this equation.

Effect of Oxygen.—The inhibiting effect of oxygen, first noted by Bunsen and Roscoe, has been verified by all subsequent workers. The main photochemical process which occurs on illumination of H_2—Cl_2—O_2 mixtures is accompanied by a sensitised formation of water. Fortunately, however, the extent to which the latter reaction takes place, even with several per cent. of oxygen present, is not great enough to depreciate the oxygen content seriously. The rate of disappearance of hydrogen is therefore practically equal to the rate of formation of hydrochloric acid, and the concentration of inhibitor is sensibly constant throughout the course of each experiment.

Chapman and MacMahon (*J.C.S.*, **95,** 959, 1909) found the sensitivity of stoichiometric mixtures of hydrogen and chlorine at atmospheric pressure to be inversely proportional to the oxygen content. This result was confirmed by Bodenstein and Dux, who, working also with practically stoichiometric mixtures and varying the partial pressure of oxygen up to 22·5 mm. Hg, found the rate of formation of hydrochloric acid to be given by

$$\frac{dx}{dt} = k\frac{[Cl_2]^2}{[O_2]}.$$

These authors suggested that the dependence of the velocity on the concentration of oxygen for any reaction mixture might be represented (cf. equation (1)) by

$$\frac{dx}{dt} = \frac{k[Cl_2]^2[H_2]}{[O_2]\{m + [H_2]\}} \quad . \quad . \quad . \quad (4)$$

Further observations have been made by M. C. C. Chapman in the paper already referred to. As a result of experiments carried out with low partial pressures of hydrogen, she concluded that oxygen is not an inhibitor unless appreciable quantities of hydrogen are present in the mixture. She states that " the rate of combination is independent of the concentration of oxygen in mixtures in which the concentration of hydrogen is very small; for all other mixtures it is inversely proportional to the concentration of the oxgyen." Combining these results with the conclusions she had already drawn regarding the stoichiometric rôles of the hydrogen and chlorine, she proposed the summarising formula

$$\frac{dx}{dt} = \frac{k[Cl_2]^2[H_2]}{a'[H_2]^{2-y}[O_2] + [Cl_2]} \quad . \quad . \quad . \quad (5)$$

as expressing the complete kinetic law. It will be observed that for very low values of $[H_2]$ this equation does degenerate to

$$\frac{dx}{dt} \propto [H_2][Cl_2],$$

i.e. the rate is independent of the oxygen content. If it be allowed that the index y in the denominator of equation (5) is unity, in other words if the retarding influence of excess of hydrogen noted by Chapman be discredited, the equation becomes

$$\frac{dx}{dt} = \frac{k[Cl_2]^2[H_2]}{a'[H_2][O_2] + [Cl_2]} \quad . \quad . \quad . \quad (5a)$$

It is not clear, however, that equation (5) does satisfactorily represent all the experimental results of Mrs. Chapman. For mixtures which are approximately equimolecular in respect of H_2 and Cl_2, she found, with Chapman and MacMahon and Bodenstein and Dux, that the velocity is inversely proportional to the oxygen content. This means that the second term in the denominator must be negligible under these conditions in comparison with the first, yet under the same conditions the order of the reaction with respect to chlorine was found to be distinctly less than two. The latter result, of course, would require that the value of the second term in the denominator is at least comparable with the first.

Thon's experimental work (*Z. physikal. Chem.*, **124,** 327, 1926) on the nature of oxygen inhibition was based on the following considerations. Equation (3)

$$\frac{dx}{dt} = \frac{k[Cl_2]^2[H_2]}{[H_2] + n[Cl_2]} \quad . \quad . \quad . \quad . \quad (3)$$

which represents the results of Bodenstein and Dux and also in large measure those of Chapman for the dependence of rate of reaction on the hydrogen and chlorine contents, could be modified to include the effect of oxygen in two ways, viz.

$$\frac{dx}{dt} = \frac{k_1[Cl_2]^2[H_2]}{[H_2][O_2] + k_2[Cl_2]} \quad . \quad . \quad . \quad (6)$$

or

$$\frac{dx}{dt} = \frac{k_1[Cl_2]^2[H_2]}{[O_2]\{[H_2] + k_2[Cl_2]\}} \quad . \quad . \quad . \quad (7)$$

The constants k and n of equation (3) then become

$$k = \frac{k_1}{[O_2]} \text{ and } n = \frac{k_2}{[O_2]}$$

in equation (6), and

$$k = \frac{k_1}{[O_2]} \text{ and } n = k_2$$

in equation (7).

In order to decide between equations (6) and (7), Thon attempted to determine how the constant n of the empirical formula (3) actually does vary with the concentration of oxygen. From the results of a number of kinetic measurements carried out with reaction mixtures containing widely different amounts of H_2, Cl_2, and O_2, he found that constancy of the k of equation (3) was best obtained in nearly every case for a constant value of $n = 0{\cdot}1$. In the complete series of experiments the concentration of oxygen was varied twenty-fold. Thon concluded from this that the coefficient n is indeed a constant independent of the concentration of oxygen, and he therefore decided between the kinetic equations (6) and (7) above in favour of the latter.

Except in one particular, an equation of the form of (7) is in agreement with the work of previous authors on the inhibiting effect of oxygen. It fails, however, to explain the already recorded statements of M. C. C. Chapman that the inhibiting effect of oxygen falls off with decreasing partial pressure of hydrogen and probably vanishes for very low concentrations of the latter gas. Rather, equation (7) assumes under these conditions the limiting form $\frac{dx}{dt} \propto \frac{[H_2][Cl_2]}{[O_2]}$ instead of Mrs. Chapman's relation $\frac{dx}{dt} \propto [H_2][Cl_2]$. Another feature of equation (7) is that it fixes no limit to the rate of photo-combination of H_2 and Cl_2 in reaction mixtures which are completely freed from oxygen. This formal objection will be discussed later. Further experiments on the inhibiting effect of oxygen have been carried out by Cremer (*Z. physikal. Chem.*, **128,** 285, 1927) in Bodenstein's laboratory. His experimental procedure was adapted for the simultaneous measurement of the rates both of hydrochloric acid formation and of water formation. A large glass reaction vessel containing P_2O_5 was connected to a quartz spiral manometer and (by a tap) to a small sample bulb. After illumination for a given time, the decrease of pressure (due to water formation) was determined and then a sample of the reaction mixture withdrawn into the sampling bulb and analysed for Cl_2 and HCl. This procedure was repeated several times for each reaction mixture until the reaction was nearly over. In this way the concentrations of H_2, Cl_2, and O_2 were determined at intervals throughout the reaction course, and it was established that the decrease in concentration of O_2 was comparatively small. It will be recalled that in the experimental arrangement of Bodenstein and Dux, the rate of HCl formation was obtained from and assumed equal to the rate of diminution of the partial pressure of hydrogen, while in the experiments of M. C. C. Chapman the rate of formation of HCl was obtained on the assumption that the decrease of pressure is due entirely to absorption of HCl. The experiments of Cremer show that in both cases no significant errors result from the assumptions. We will discuss later Cremer's results for the velocity of the sensitised formation of water in H_2—Cl_2—O_2 mixtures, and only consider now his data on the inhibition by O_2 of hydrogen chloride formation. The initial total pressure of the system in all experiments was about atmospheric, the partial pressure of the hydrogen was slightly greater than that of the chlorine, and the initial partial pressure of oxygen was varied between 24 mm. and 166 mm. In each single experiment the Bodenstein-Dux relation

$$\frac{d[HCl]}{dt} = k_D \frac{[Cl_2]^2}{[O_2]}$$

was obeyed, i.e. the value of k_D in each experiment was constant. In different experiments, however, k_D was found not to be constant, but to increase with increasing partial pressure of oxygen. Cremer found that the coefficient k_C calculated on the basis of the empiric equation

$$\frac{d[HCl]}{dt} = k_C \frac{[Cl_2]^2[H_2]}{[Cl_2] + 0{\cdot}02[H_2][O_2]} \quad . \quad . \quad . \quad (8)$$

was constant from experiment to experiment, independent of the oxygen content, and he considered this equation to be the best expression of his results. On the basis of this formula the constants k_C fall into two groups, relating to experiments with different fillings of P_2O_5 in the experimental tube. Cremer drew the inference that the reaction velocity is very sensitive to surface influences. Unfortunately only seven experiments were carried out in all, and it is possible that other equations beside (8) would fit the results equally well. The question of a possible surface influence is of importance and it cannot be regarded as definitely settled by these experiments alone. It may be mentioned that Thon has suggested this same possibility as a means of accounting for the discordant results of Chapman and Bodenstein and Dux, and Cremer thinks that to a catalytic surface reaction may also be ascribed the difference between his own and Thon's results.

Summing up the work of different investigations on the rôles of H_2, of Cl_2, and of O_2 in the hydrogen-chlorine reaction, it will be apparent that discrepancies of a major kind exist. No one equation yet suggested is sufficiently comprehensive to embrace the experimental results of all investigations. Two equations have, however, been advanced, each of which is partially successful. These are

$$\frac{d[HCl]}{dt} = \frac{k_1[Cl_2]^2[H_2]}{[H_2][O_2] + k_2[Cl_2]} \quad . \quad . \quad . \quad . \quad I$$

$$\frac{d[HCl]}{dt} = \frac{k_1[Cl_2]^2[H_2]}{\{[H_2] + k_2[Cl_2]\}[O_2]} \quad . \quad . \quad . \quad . \quad II$$

Equation I was advanced by Thon in his theoretical paper (*Fortschritte der Chemie*, Heft 11, 1926), and is a modification of that put forward by M. C. C. Chapman. In the equation of the latter the $[H_2]$ in the denominator was raised to a power slightly greater than 1·5. Equation II in a slightly different form was originally adopted by Bodenstein and Dux, and was later advocated by Thon on the completion of his own experimental work on the reaction. Equation II is compatible with all the experimental results hitherto obtained except

(1) Mrs. Chapman's observation that oxygen ceases to inhibit the reaction at low partial pressures of hydrogen ;
(2) Cremer's results with high oxygen concentrations.

It should also be observed that Thon's value (0·1) for k_2 is not quite in agreement with the results of M. C. C. Chapman regarding the order of reaction with respect to Cl_2. A value for k_2 nearer 0·5 seems to be indicated from her data.

With regard to equation I, this is incompatible with Thon's results and as already mentioned it is not consonant with all the observations of Mrs. Chapman. It is also not clear how Cremer's observations, which in general conflict with equation II, are to be fitted in on the basis of equation I with the results of other workers in whose experiments much less oxygen was employed. Cremer puts $k_2 = 50$, but this value is much too high to permit of equation I degenerating to the Bodenstein-Dux $[Cl_2]^2$ law in cases where the partial pressure of oxygen is less than 10 mm. For such low concentrations of oxygen and so long as $H_2 > \frac{1}{4}[Cl_2]$, the $[Cl_2]^2$ law seems to be well established not only by the experiments of Bodenstein and Dux themselves but by those of Kornfeld and Müller (*Z. physikal. Chem.*, **117**, 242, 1925). Thon originally suggested that discrepancies of this nature might be due to an unappreciated dependence of the value of k_2 upon the experimental conditions of observation. However, even if in equation I or equation II we allow for such a variation in the value of this coefficient from author to author, we still find that neither equation embraces all the recorded observations. A more complex expression of the kinetic law seems necessary, of a form which would include equations I and II as different limiting cases under conditions as yet not properly understood.

Sensitised Formation of Water in Hydrogen-Chlorine Mixtures Containing Oxygen.—We have seen that the marked inhibitors of hydrogen-chlorine combination (such as NCl_3 and O_3) are removed during the induction period ; the destruction of such impurities is complete before appreciable formation of HCl sets in. The much feebler inhibiting effect of oxygen is also connected with its removal to form water, but this reaction occurs slowly compared with the destruction of strong inhibitors, and the oxygen concentration does not change by a great amount even while the hydrogen-chlorine reaction completes itself. That water formation takes place on insolating H_2—Cl_2—O_2 systems was first demonstrated by Weigert (*Ann. Physik*, **24**, 243, 1907). On illuminating a mixture of 50 per cent. H_2, 25 per cent.

Cl_2, and 25 per cent. O_2 with a quartz mercury vapour lamp, he found that about 40 per cent. of the hydrogen was converted into water, the chlorine being at the same time quantitatively converted into HCl. The kinetics of this water-forming reaction are of considerable importance for the theory of hydrogen-chlorine combination. Only in the presence of smaller or greater quantities of oxygen has the latter reaction so far been studied, and it is necessary that the assumptions which underlie any reaction scheme from which the kinetics of hydrogen-chlorine combination may be derived should not be in disagreement with the assumptions necessary to account for the rate of simultaneous water formation. Unfortunately, however, just as for the kinetics of H_2—Cl_2 combination, the results of different investigators on the velocity of the sensitised formation of water do not agree. The reaction was first studied quantitatively by Norrish and Rideal (*J.C.S.*, **127**, 787, 1925). They employed a glass reaction vessel containing a layer of phosphorus pentoxide to absorb the water formed, and they measured the decrease of pressure (due solely to water formation) by a mercury manometer. They used a rather intense light source—a quartz mercury lamp placed close to the reaction vessel—and worked with mixtures at a total pressure of one atmosphere. From the slope of their pressure-time curves they determined the *initial* rate of water formation in reaction mixtures of known composition. It was found that, with light of constant intensity, this initial rate is given by the relation

$$\frac{d[H_2O]}{dt} = k[Cl_2][O_2],$$

and is independent of the partial pressure of the hydrogen between the limits 0·16 to 0·9 of the total pressure. Presumably, the coefficient k is proportional to the incident light intensity, although no experiments were made to test this point. A different kinetic law was obtained by Cremer in the experiments already described (p. 528). Working with a smaller light intensity and with lower oxygen contents than Norrish and Rideal, Cremer found the rate of water formation to be given by

$$\frac{d[H_2O]}{dt} = k[Cl_2],$$

i.e. the rate is independent of both the hydrogen and oxygen concentrations. In spite of the small pressure changes observed and consequent lack of accuracy in Cremer's measurements, his results appear to be irreconcilable with those of Norrish and Rideal, unless the differences are due to the different conditions (light intensity, wavelength) obtaining in his work. Both researches, however, establish the fact that under the usual conditions of investigation of H_2—Cl_2 combination (high sensitivities and comparatively low $[O_2]$), the change in the concentration of inhibiting oxygen is quite negligible throughout the greater part of the reaction course.

The Rôle of Water Vapour in the H_2—Cl_2 Reaction.—The work of Baker has been instrumental in directing attention to a possible influence of water on chemical reactivity in general, and the question has become one of some theoretical importance. The hydrogen-chlorine reaction is one of those processes in which water vapour plays a prominent part, and the interpretation of the phenomenon has been the subject of much discussion and many divergent views. Baker (*J.C.S.*, **65,** 611, 1894) and Mellor and Russell (*ibid.*, **81,** 1272, 1902) found that after long drying over P_2O_5 a mixture of hydrogen and chlorine no longer explodes on exposure to direct sunlight, but that only slow combination occurs. Bodenstein and Dux (*Z. physikal. Chem.*, **85,** 297, 1913) found that less drastic methods of drying had no influence on the velocity of combination. For partial pressures of water vapour between 2·3 mm. and 0·004 mm., the reaction velocity was found to be independent of p_{H_2O}. They suggested that Mellor and Russell's result might possibly be ascribed to an inhibiting effect of oxygen, previously adsorbed on to the P_2O_5 (which was prepared by distillation in a stream of oxygen) and subsequently liberated into the gas mixture. The effect of thorough desiccation was carefully investigated with a different technique by Coehn and Tramm (*Z. physikal. Chem.*, **105,** 356, 1923; *Ber.*, **56,** 458, 1923) and Coehn and Jung (*Z. physikal. Chem.*, **110,** 705, 1924; *Ber.*, **56,** 696, 1923). Here purification and drying of the reacting gases was effected by liquefaction and fractional distillation. Employing high vacua and well baked-out apparatus, it was found possible to prepare a gas mixture whose water content was estimated to be below 10^{-7} mm. Hg. Gas mixtures containing higher partial pressures of water vapour (for example 10^{-5} mm.) could be prepared by leaving the apparatus for some time in connection with a bulb containing ice maintained at a suitable low temperature. They found that with a very thoroughly desiccated mixture of H_2 and Cl_2 ($p_{H_2O} < 10^{-7}$ mm. Hg) no combination is detectable on exposure to direct sunlight for twenty days. With a partial pressure of water vapour of the order 10^{-5} mm., however, appreciable reaction is observed under the illumination of a 100 c.p. lamp within a few minutes. On the other hand, if the very dry gas mixture is contained in a quartz apparatus and exposed to the ultra-violet radiation of a quartz mercury vapour lamp, combination is complete within an hour. From the standpoint of the mechanism of reaction which will be dealt with later, the quantum efficiency of this photo-combination of the dry gases in ultra-violet light is of interest. In sharp contrast to the very high values (*circa* 10^5) of the quantum yield which characterise the normal process in visible or ultra-violet light, Coehn and Heymer (*Naturwiss.*, **14,** 299, 1926) have found that the quantum yield with the highly desiccated gases in ultra-violet light is less than seven. Hence, in ultra-violet light also, the course of reaction is very markedly dependent on the water vapour content of the system. Thon (*loc. cit.*, p. 69) suggests that the presence of moisture may be as necessary for reaction in ultra-violet light as in the visible, and that the small amount of photo-combination of "dry" H_2 and Cl_2 in ultra-violet light may be conditioned by a preliminary sensitised formation of H_2O vapour from the trace of oxygen present in the system.

Of considerable theoretical significance is the value to which the partial pressure of water vapour can be reduced before the quantum efficiency of the photo-combination in visible light is appreciably affected. The experiments of Coehn and co-workers have established that in the region of very low water content—$p_{H_2O} < 10^{-7}$ mm.—reaction does not take place in visible light, and that above an incompletely defined value of the partial pressure of water vapour, the light sensitivity of the system becomes independent of the water content. This limiting value apparently lies above 10^{-5} mm. Hg, but a sufficient number of experiments were not carried out to fix it more exactly. The work of Bodenstein and Dux indicates that decrease in the partial pressure of water vapour down to 0·004 mm. does not affect the velocity of reaction. However, Cathala (*Bull. Soc. chim.*, **39,** 612, 1926) and Lewis and Rideal (*J. Amer. Chem. Soc.*, **48,** 2553, 1926) have pointed out that several unconsidered factors—in particular, the sensitised formation of water from the oxygen present in the system—might possibly contribute to make the partial pressure of H_2O vapour actually present in Bodenstein and Dux's experiments considerably greater than these authors presumed. The actual nature of the dependence of the reaction velocity upon the partial pressure of water vapour in the intermediate region between 10^{-7} mm. and 10^{-1} mm. Hg must, therefore, be regarded as unsettled.

The Action of Light on Chlorine and on Chlorine-Water Vapour Systems.—Before considering the various mechanisms proposed for the hydrogen-chlorine reaction itself, it is necessary to deal with the properties of illuminated chlorine in the presence and in the absence of moisture, the nature of the primary process, and the possible chemical reactions which occur in such systems. The problems arising in this connection, however, have so far resisted adequate solution, an issue necessary before an insight into the complex hydrogen-chlorine reaction and other photochemical reactions of chlorine may be attained.

The nature of the *primary* process in illuminated chlorine (and in the other halogens) is of special importance, and is rendered more complex by the problem as to whether or not it may be profoundly modified by the presence of impurities, in particular, of water vapour. A number of different theories have been advanced by photochemists and physicists with regard to this primary process; among them are the following:—

(1) Bodenstein's original view (1913) of *ionisation*, i.e. formation of Cl_2^+ and an electron. This hypothesis was soon abandoned, as well-authenticated experiments (see p. 448) show that comparatively few free electrons are present in illuminated Cl_2 and also the energy supplied by the radiation is not sufficient to effect the postulated change.

(2) The formation of an *activated molecule* (Bodenstein, *Z. Elektrochem.*, **22,** 53, 1916) by partial separation of a valency electron, a concept previously advanced by Volmer (*Z. Elektrochem.*, **21,** 113, 1915). This idea was strongly supported by Stern and Volmer (*Z. wiss. Phot.*, **19,** 275, 1920), whose views influenced theoretical speculation for several years. Stern and Volmer considered that even when the energy of the quantum absorbed is greater than the heat of dissociation of the absorbing molecule, the primary light process is always the "activation" of the molecule, and that subsequent collision is necessary before dissociation can occur. They employed the following arguments against the view that the primary process for chlorine is a dissociation into atoms.

(α) Combination of H_2 and Cl_2 takes place with light of frequency less than that corresponding to the heat of dissociation of $Cl_2(D_{Cl_2})$. More recent work shows, however, that D_{Cl_2} is much less than the value accepted in 1920, and that actually the limiting frequency is at least not very far removed from that corresponding to the heat of dissociation of Cl_2. This question is discussed later (p. 538).

(β) In the case of iodine, it is known that this substance can absorb and re-emit as a resonance spectrum light of wavelength 1849 Å, i.e. energy corresponding to many times the heat of dissociation, without dissociation occurring.

(γ) Many gases do not absorb sensibly in the region which corresponds to the energy of dissociation.

More recent work shows, however, that while such statements as (β) and (γ) are true, the conclusion of Stern and Volmer is not inevitable.

(3) *Dissociation into Atoms.*—Primary dissociation of the absorbing molecule was assumed by Warburg in all reactions investigated by him and in which such dissociation was energetically allowable. The assumption appears to have been applied to the photochemistry of chlorine first by Nernst (*Z. Elektrochem.*, **22,** 53, 1916; *ibid.*, **24,** 335, 1918; *Physikal. Z.*, **21,** 602, 1920), and this view has been adopted by many subsequent investigators. The Nernst view of the primary process was direct dissociation of Cl_2 by light into two normal atoms, but more recent work favours dissociation into an activated and a non-activated chlorine atom by light of wave-length lower than the convergence limit.

According to Franck and Kuhn's analysis of the band spectrum of Cl_2 (cf. p. 221), we may conclude that (1) for wave-lengths less than 4785 Å (region of continuous absorption) the primary result of absorption is the dissociation of the chlorine molecule into a normal atom and an activated atom—the latter internally excited to the extent of 2500 cal. per gm.-atom (0·11 volt); (2) any excess of absorbed energy over that required to effect the primary process appears as kinetic energy of translatory motion of the separating atoms, and Franck and Hogness (*Z. Physik*, **44,** 26, 1927) suggest that this kinetic energy may be of significance in photochemical reactions of chlorine; (3) for absorption of light of wave-lengths greater than 4785 Å the primary process consists of an activation of the chlorine molecule.

In connection with the two main theories of the action of light on chlorine, activation and primary dissociation, it was, of course, early recognised that even on the Stern-Volmer view dissociation of chlorine could occur on subsequent collision of an activated Cl_2 molecule. Thus, Coehn and Jung (*Z. physikal. Chem.*, **110,** 705, 1924) postulated that after a primary process $Cl_2 + h\nu \rightarrow Cl_2^*$, the reaction $Cl_2^* + Cl_2 \rightarrow Cl_2 + 2Cl$ takes place, and that the hydrogen-chlorine reaction involves the chlorine atoms so formed. Although the question of the nature of the primary process in illuminated chlorine is of great importance, it is—from a chemical standpoint—subordinate to the question as to whether the reacting entities in photochemical reactions of chlorine are chlorine atoms or activated chlorine molecules. If the physical evidence derived from a study of the absorption spectrum of chlorine be accepted, naturally chlorine atoms must be a reacting species; again, if the Stern-Volmer view be taken, and it is agreed that the adjustments in internal energy of the activated chlorine molecule necessary for dissociation take place when Cl_2^* molecules collide with any molecular species (e.g. Cl_2 or H_2), we arrive at the same view. Unless the activated chlorine atoms formed on Franck's theory of the primary process have properties chemically very different from those of normal chlorine atoms, the differences between the two views are not very pronounced and consist mainly in the time elapsing between the electron jump and the dissociation. On the first hypothesis of primary dissociation, the time between the absorption of a quantum and splitting of the molecule is less than 10^{-12} sec.; in the second case, it is the average time between collisions, which at room temperature and atmospheric pressure is $10^{-9} - 10^{-10}$ sec. On the other hand, the view has been taken that activated chlorine may have a comparatively long life, considerably greater than $10^{-7} - 10^{-8}$ sec., and that in the combination of hydrogen and chlorine it is the activated chlorine molecules which react.

Apart from these two main theories of the primary action of light in H_2—Cl_2 combination, other theories of a more specialised type have from time to time been proposed. Among these are the theories of Norrish (*J.C.S.*, **127,** 2317, 1925) and of Weigert (*Z. physikal. Chem.*, **106,** 407, 1923). The former located the primary action on an adsorbed water film on the walls of the reaction vessel, but the theory has been disproved by the experiments of Coehn and Heymer (cf. p. 519). Weigert has interpreted absorption leading to photochemical reaction as an "inner photoelectric effect," i.e. in the case of the hydrogen-chlorine reaction as the bridging of an H_2 and a Cl_2 molecule by an electron jump, thus $Cl_2 + h\nu + H_2 \rightarrow \underbrace{Cl_2^- + H_2^+}$.† The reactive species is then the activated, optically-coupled complex so formed, the subsequent reaction suggested being

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† It will be observed that, in this theory of Weigert, the hydrogen molecule is regarded as the "electron-giver," the Cl_2 as "electron-catcher." Thus,

$$\underbrace{\mathrm{Cl_2^-} + \mathrm{H_2^+}} \rightarrow \mathrm{HCl} + \mathrm{H} + \mathrm{Cl},$$

followed by the Nernst chain. As pointed out by Thon (*Fortschritte der Chemie*, **18,** Heft 11, 1926), this theory is open to the objection that it could easily permit of a difference between photochemical and optical extinctions, shown by Burgess and Chapman to be non-existent.

Of considerable significance for the theory of the photochemistry of chlorine, including the hydrogen-chlorine reaction, are (α) experiments on the Budde effect, (β) attempts to "activate" Cl_2 in the absence of H_2 or other acceptor and attempts to determine the life of the "active" product, (γ) the question as to whether or not definite wave-length limits for photochemical action exist, and (δ) though possibly of minor importance, cloud formation in moist illuminated chlorine. The Budde effect is of interest in relation to the different sensitivites (to visible light) of damp and very dry mixtures of hydrogen and chlorine discovered by Coehn and his co-workers. The Budde effect—the expansion of chlorine or of bromine on illumination—was discovered for both gases by Budde (*J. pr. Chem.*, **7,** 376, 1873). Later work by Richardson (*Phil. Mag.*, [v], **32,** 277, 1892) and Bevan (*Proc. Roy. Soc.*, **72**A, 5, 1903) on chlorine, and by Ludlam (*Proc. Roy. Soc. Edin.*, **34,** 197, 1924) on bromine proved that the expansion is due entirely to the conversion of the absorbed light energy into heat. The experiments of Baker (*British Association Reports*, p. 496, 1894), Mellor (*J.C.S.*, **81,** 1280, 1902), and Shenstone (*ibid.*, **71,** 471, 1897) showed that the expansion is appreciable only in damp chlorine (or bromine) and that dry chlorine shows little or no Budde effect. A quantitative study of the Budde effect in Br_2 containing small amounts of water vapour has recently been made by Lewis and Rideal (*J.C.S.*, pp. 583, 596, 1926). Using light of wave-length 540-570 $\mu\mu$ they studied the dependence of the Budde effect on the partial pressures of Br_2 and of H_2O, as well as on the surface area illuminated, and concluded that only a definite hydrate of composition $Br_2 . H_2O$ is photoactive, and that light absorbed by Br_2 molecules is re-emitted as fluorescence. According to Lewis and Rideal, this hydrate is strongly adsorbed on glass surfaces; its bulk concentration is thus very small, but correspondingly its absorption coefficient is calculated to be enormously large. A distinct difference in the absorption spectra of dry and moist bromine was found by these authors in measurements over the range 610 — 510 $\mu\mu$. Especially between 610 $\mu\mu$ and 560 $\mu\mu$ is the difference marked. Wet bromine commences to show a definite absorption at 610 $\mu\mu$, but the dry bromine

he believes that, although hydrogen itself has an absorption band only in the far ultra-violet, a hydrogen molecule in the neighbourhood of a chlorine molecule (which has a large electron affinity) may be made to lose an electron by light of much smaller frequency.

shows no marked absorption at wave-lengths longer than 570 $\mu\mu$. Rideal and Lewis assume that with moisture and thus the hydrate $Br_2 . H_2O$ present, dissociation into bromine atoms occurs on illumination with light of any wave-length less than 610 $\mu\mu$, and that the Budde effect is the warming of the gas due to the heat of recombination of the bromine atoms. On the other hand, in absence of moisture, when no Budde effect is observable, they suggest that the light absorbed is only re-radiated as fluorescence, and that thus water influences the primary action of light on bromine. The same view has been taken by Weigert (*Z. physikal. Chem.*, **106,** 426, 1923) in respect of the primary action of light on Cl_2 and in the H_2—Cl_2 reaction. In agreement with a previous suggestion of Mellor (*J.C.S.*, **81,** 1293, 1902), he regards the presence of water molecules (or molecules of certain other dipole substances) as necessary before the conversion of radiant energy into chemical energy or into heat energy (Budde effect) occurs. In the case of the H_2—Cl_2 reaction, Weigert assumed the primary process to be an inner photoelectric effect in an H_2—Cl_2 complex, which, however, takes place only in the presence of H_2O, so that actually the photosensitive constituent of the system was taken to be a complex $(Cl_2)_x(H_2O)_y(H_2)_z$, a suggestion also previously advanced by Bevan (*loc. cit.*). Thon also considers water to influence the primary process, a view to be sharply differentiated from other theories, which place the action of water at a later stage in the process, that is, in the chain mechanism.

Reverting to experiments on the Budde effect, which, according to Lewis and Rideal and to Weigert, support the view of a " physical " action of H_2O on the primary process, it is to be noted that in the case of bromine the Budde effect is detectable—in the damp gas—with light of wave-lengths up to 580 $\mu\mu$, while according to Kuhn's measurements (*Z. Physik*, **39,** 77, 1927) the convergence limit lies at 5107 Å. The heat of dissociation of bromine (into normal atoms) has been determined both by chemical methods and from optical measurements. The former give for D_{Br_2} 46,200 cal. (Landolt-Börnstein, *Tabellen*, 5th edition), the latter 45,200 cal. (Kuhn, *loc. cit.*). Taking the mean value 45,700 cal., we find that light of wave-lengths in the interval between 511 $\mu\mu$ (the convergence limit) and 622 $\mu\mu$ may cause secondary dissociation of bromine into normal atoms, the actual dissociation resulting from a collision of the activated bromine molecule (the primarily formed resultant of the light absorption) with some other molecule. Rideal and Lewis used light of 540-570 $\mu\mu$ in their experiments on the Budde effect, i.e. in the region of band absorption referred to ; it would be of interest to determine the Budde effect in wet and in dry bromine with light of wave-lengths on the short wave side of the convergence limit (511 $\mu\mu$).

It is seen that that both in Lewis and Rideal's and in Weigert's theory of the action of light on the halogens, the assumption is made that the pure *dry* gases emit the absorbed radiation as fluorescence. Direct tests made by Kistiakowsky (*J. Amer. Chem. Soc.*, **49,** 2194, 1927) on pure chlorine, carefully dried, showed that only a very small fraction, if any, of the absorbed light is re-emitted as fluorescence. He also found that the structure of the absorption spectrum and the total absorption of chlorine are not appreciably altered by extreme drying. As in the case of bromine, however, there appears to be no doubt * regarding the decrease in the Budde effect on drying chlorine, and the absence of fluorescence in illuminated chlorine must be regarded as irreconcilable with the theories of Weigert and of Rideal and Lewis. We are thus practically forced with Kistiakowsky to the conclusion that light of suitable wave-length dissociates chlorine into atoms, independently of the presence of water vapour, and that the process of recombination of the atoms is—in the absence of water vapour—very slow in the gas phase and takes place practically entirely on the dry walls of the reaction vessel. The heat of reaction will thus be transported away by the walls, and little or no Budde effect will be observed. On the other hand, with water vapour present, either the wall process is poisoned or the homogeneous reaction is catalysed, the heat of reaction appears in the gas, and the Budde effect is observed. Experiments on the Budde effect are thus not decisive as to the action of water on the primary process in illuminated chlorine. Different interpretations of the influence of water on the manner of transformation of the absorbed radiant energy have been upheld. Further work is necessary before the mechanism of the Budde effect in damp Cl_2 and Br_2 can be regarded as settled.

In connection with the action of light on chlorine, experiments on the variation of quantum yield in the H_2—Cl_2 reaction with wave-length and the determination of the threshold frequency (if any exists) are of importance. According to Franck and Kuhn, the primary process for wave-lengths shorter than the convergence limit 478·5 $\mu\mu$ is a dissociation into an activated and a non-activated chlorine atom, while for wave-lengths longer than this (in the band absorption) the primary process is to be regarded as an activation of the chlorine molecule. The subsequent fate of this activated molecule depends on its life period, its environment, and its energy content. Assuming an average life of $10^{-7} - 10^{-8}$ sec., the possibility of re-radiation of the absorbed energy as fluorescence will only be appreciable for low total pressures of the system. Normally, however, the activated molecule *may* suffer many collisions before it spontaneously fluoresces. On collision, the excess energy of the activated molecule may be dissipated as heat energy of the colliding units, or if its excess energy, although less than 59,400 cal. per mole (corresponding to 478·5 $\mu\mu$), is greater than the heat of dissociation of chlorine 57,700 cal. (corresponding to light of 493 $\mu\mu$), dissociation into normal atoms may still occur as a secondary process. Even if the internal energy of the activated chlorine molecule lies below the heat of dissociation, the possibility remains that the deficiency might still be supplied by the energy of relative motion of the colliding units, though at ordinary temperatures the probability of this taking place is small. We might conclude, therefore, that the formation of atoms in illuminated chlorine—either by a primary or by a secondary process—is possible only for wave-lengths up to about 500 $\mu\mu$, and hence, if the hydrogen-chlorine reaction necessarily involves chlorine atoms at some stage, a threshold wave-length should then be found at about this figure. The absorption spectrum of chlorine in the photochemically active region appears, in the absence of very strong dispersion, as a continuous absorption band with a minimum at about 580 $\mu\mu$, at which point, however, there is still a small but definite absorption. Fig. 48 is a plot of the accurate data of von Halban and Siedentopf (*Z. physikal. Chem.*, **103,** 71, 1922), showing the logarithm of the extinction coefficient at wave-lengths between 254 $\mu\mu$ and 643 $\mu\mu$. Coehn and Jung (*Z. physikal. Chem.*, **110,** 705, 1924) claimed to have experimentally established a threshold frequency for the hydrogen-chlorine reaction corresponding to a wave-length of 540 $\mu\mu$. They filled eight tubes with damp stoichiometric mixtures of hydrogen and chlorine, illuminated each for the same time with different portions of the visible spectrum, and determined the amounts of hydrochloric acid formed. They inferred from these results that a true threshold at 540 $\mu\mu$ exists, i.e. that light of longer wave-length is ineffective in producing HCl, but their interpretation has been

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* This statement cannot now be regarded as correct, since recent work by Brown and Chapman (*J.C.S.*, p. 560, 1928) has failed to confirm the observations of Lewis and Rideal. Thorough drying of bromine by P_2O_5 was found by Brown and Chapman to be unaccompanied by any decrease in the magnitude of the Budde effect. Also for chlorine, Martin, Cole, and Lent (*J. Physical Chem.*, **33**, 148, 1929) find that the Budde effect is not greatly diminished by careful purification and drying of the gas.

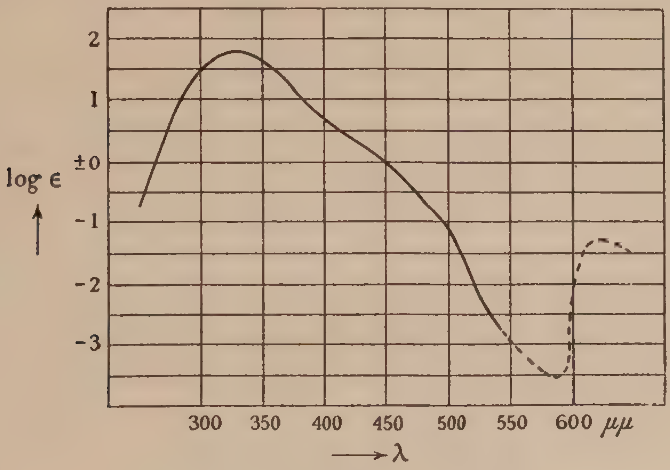

FIG. 48.—Absorption spectrum of chlorine.

criticised by Bowen (*Phil. Mag.*, [vi], **50,** 879, 1925). The latter shows that their results only prove that rate of combination is proportional to the amount of light absorbed. W. Taylor (*Phil. Mag.*, [vi], **49,** 1165, 1925) found the critical wave-length to be 490 $\mu\mu$, but a similar criticism of this result has also been made by Bowen. Padoa and Butironi (*Atti. R. Accad. Lincei*, [v], **25,** ii, 215, 1916) find that combination of the mixed gases occurs using light of wave-length 530-550 $\mu\mu$, while recently Weigert and Nicolai (*Trans. Faraday Soc.*, **21,** 581, 1926) have claimed that the higher wave limit of the interaction of hydrogen and chlorine is nearly 590 $\mu\mu$, i.e. a position approximating to the minimum on the absorption curve of von Halban and Siedentopf. If this result is substantiated, any wave-length in the violet band of chlorine, but none in the red band,* activates chlorine sufficiently to enable it to react with hydrogen. If this is the case, it would appear that dissociation of chlorine into atoms is not an *essential* preliminary to its combination with hydrogen.

The effect of variation of wave-length on quantum yield in the hydrogen-chlorine reaction has not been quantitatively investigated —doubtless owing to difficulties in reproducing constant conditions in respect of concentration of inhibitors. There appear, however, to be some grounds for the belief that the quantum yield diminishes with increasing wave-length. Weigert and Nicolai (*loc. cit.*) have stated that this is the case, without, however, indicating the nature of their experimental evidence, and the recent results of Taylor and Elliot (*Trans. Faraday Soc.*, **23,** 583, 1927) conform to the view that between 350 $\mu\mu$ and 550 $\mu\mu$ the effective photochemical equivalent (moles of photolyte decomposed per calorie of radiation absorbed) is independent of the wave-length, or, in other words, the quantum yield decreases with increasing wave-length. We must thus assume that the number of molecules effectively activated per quantum absorbed or the length of the chain or both factors together increase with increasing frequency. Weigert (*loc. cit.*) suggests that the first factor is the important one, and that either preliminary thermal activation of Cl_2 is necessary when long wave radiation is used, or the " red " band overlaps the photochemical " violet " band, so that the longer the wave-length of the light the greater is the percentage of radiation absorbed thermally.

Many experiments have been made to determine the life of the activated state in insolated chlorine by pre-illuminating chlorine in the absence of an acceptor, passing the gas into hydrogen in the dark, and determining whether any reaction takes place. Such experiments have, in general, yielded negative results, showing that the life of the activated state is small. Le Blanc and Volmer (*Z. Elektrochem.*, **20,** 494, 1914) and Bodenstein and H. S. Taylor (*ibid.*, **22,** 202, 1916) showed that, following an interval of $\frac{1}{1000}$ — $\frac{1}{1500}$ sec. after illumination of the chlorine, no hydrochloric acid is formed on bringing the gas into contact with hydrogen. The same negative result was obtained by Wendt, Landauer, and Ewing (*J. Amer. Chem. Soc.*, **44,** 2377, 1922) after an interval of 0·01 sec. These authors used a powerful quartz mercury lamp to activate the chlorine ; equally fruitless were attempts using high potential electric discharges. Taylor's result has been subjected to analysis by Göhring (*Z. Elektrochem.*, **27,** 516, 1921) and by Warburg (*ibid.*, **27,** 139, 1921) from the standpoint of testing whether it is compatible with the Nernst chain theory of the hydrogen-chlorine reaction. Chlorine atoms—if formed as postulated by this theory—should possess a relatively long life, which, however, depends on the oxygen content of the system. Göhring showed that Taylor's result of no perceptible combination of the two gases at a period of 0·00065 sec. after illumination of the chlorine is not inconsistent with the formation of chlorine atoms on insolating chlorine. Assuming that each quantum absorbed forms two chlorine atoms, that a fraction $1{\cdot}5 \,.\, 10^{-3}$ of the impacts between Cl and O_2 removes the former by formation of ClO_2 molecules, and that the chlorine used by Bodenstein and Taylor contained 0·1 per cent. O_2, Göhring* calculated that the concentration of chlorine atoms at the steady state on illumination was $3{\cdot}4 \,.\, 10^{-11}$ gm.-atom per litre, and that after a time interval of $\frac{1}{1600}$ sec. in the dark the concentration was reduced to $1{\cdot}5 \,.\, 10^{-12}$ gm.-atom per litre. If each atom of chlorine forms even as many as 10^6 molecules of HCl when the gas is led into hydrogen, the concentration of HCl in the resulting gas would only be 0·0034 per cent. which is an undetectable quantity under the experimental conditions of Bodenstein and Taylor. A similar calculation was carried out by Warburg (*loc. cit.*) *on the assumption that no oxygen was present in the chlorine*. Under these conditions, hydrochloric acid formation should be observed if the Nernst chain theory holds. Thus, even assuming that every collision between chlorine atoms results in recombination, the stationary concentration of chlorine atoms in the experiments of Bodenstein and Taylor would be $1{\cdot}96 \,.\, 10^{-9}$ gm.-atom per litre, and after $\frac{1}{1600}$ sec. this would only be reduced to $1{\cdot}8 \,.\, 10^{-9}$ gm.-atom per litre. If chlorine can be prepared free from inhibitors, it would thus be expected that in experiments of the type described hydrogen chloride formation should be observable if the Nernst theory is valid. The experiment was attempted by Marshall (*J. Physical Chem.*, **30,** 757, 1926), who fractionated chlorine by distillation under high vacuum, and prepared a gas whose oxygen content must have been very low. This was illuminated in a quartz tube by the light of a quartz mercury arc, and the chlorine then passed through a darkened capillary tube into pure hydrogen. The time of passage through the capillary was 0·00033 sec. (in other experiments 0·00020 sec.). No hydrochloric acid was detected in the resulting mixture of hydrogen and chlorine. In these experiments the chlorine was—owing to its method of preparation—exceedingly dry, and it was thought that the absence of combination of hydrogen and chlorine might be due to this cause. Further experiments were therefore carried out in which the chlorine was moistened before illumination and passage into hydrogen, but still no detectable amount of hydrogen chloride was produced. In discussing this result, Marshall points out, however, that it is not conclusive evidence against the chain mechanism of Nernst, since the combination of chlorine atoms may be catalysed by the walls of the capillary tube.

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* On the other hand, it is possible that in the case of other photochemical reactions of chlorine light in the red absorption band may initiate reaction. Thus von Halban (*Trans. Faraday Soc.*, **21**, 582, 1926) quotes the experiments of Muhr (*Thesis*, Zürich, 1922), according to which the reaction between chlorine and toluene is sensitive to red light.

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* The figures actually given are those of the later calculations of Marshall (*J. Physical Chem.*, **30**, 757, 1926).

The above-mentioned authors all obtained negative results; "activation" of chlorine for subsequent reaction in the dark, though not specifically for reaction with hydrogen, has been claimed by Venkatamariah (*J. Physical Chem.*, **27**, 74, 1923), who employed both electrical discharges and the radiation of an iron arc. "Activation" of the chlorine issuing from the chamber in which the energy was supplied was tested for in a variety of ways, among these being reaction with sulphur to form S_2Cl_2 and reaction with benzene and with acetic acid. Using the ultra-violet emission of an iron arc, a very slow production of "active" chlorine was claimed. Schaum and Feller (*Z. wiss. Phot.*, **23**, 66, 1925) used only electrical discharges of various kinds to activate the chlorine. They found that chlorine thus activated reacts more readily in the dark with toluene than does ordinary chlorine, especially as regards substitution in the side chain. The increased rate of reaction caused by "activation" was still detectable at a distance of 20 cm. from the discharge when the gas was passed through a tube of 2 cm. diameter at a rate of 3 litres an hour. Venkatamariah believes that his results point to the existence of a complex chlorine molecule of the type Cl_3, and Schaum and Feller discuss the same possibility. The work of Wendt and his co-workers, who also employed electric discharges, shows that if reaction with H_2 be taken as the criterion of the presence of such a complex, its life must be less than 0·01 sec., and hence the results of Schaum and Feller must be ascribed to other causes.

Yet the "chlor-ozone" molecule postulated above has recently been suggested as an intermediate product in the photochemical union of hydrogen and chlorine. This hypothesis, first advanced by Göhring (*Z. Elektrochem.*, **27**, 516, 1921), has been supported by Thon and by Cremer in publications from Bodenstein's laboratory. It has also been applied to the kinetics of a thermal reaction of chlorine—the reaction with carbon monoxide—in particular by Christiansen (*Inaugural Dissertation*, Copenhagen, 1921) and by Bodenstein and Plaut (*Z. physikal. Chem.*, **110**, 399, 1924).

Theories of Reaction Mechanism.—It will be apparent from the foregoing discussion that a satisfactory theory of the mechanism of the photo-combination of hydrogen and chlorine cannot yet have been established. On the other hand, many theories have been advanced, and it is hardly an exaggeration to say that no two workers in this field hold the same views with regard to the theoretical interpretation of this reaction. The complex nature which the true kinetic law assumes, together with the lack of agreement among various investigators regarding the actual form of this law, represents only one aspect of the difficulties which one meets in attempting a decision between rival hypotheses regarding the mechanism of the change. Further obstacles to the setting up of a satisfactory reaction scheme are connected with (*a*) the remarkable effects of small traces of water vapour on the rate of reaction; (*b*) the nature of the reactions which occur when destructible inhibitors are present; and (*c*) the necessity for correlating the assumptions made regarding the primary and secondary processes in H_2—Cl_2—O_2—H_2O mixtures with the experimental data of other photo- (and possibly also thermal) reactions of chlorine. It cannot yet be said that we are nearing solution of the problems arising in any of these cases. In what follows the discussion is confined to recent theories of the reaction. An exhaustive treatment is not attempted,* attention being concentrated on what are regarded as the most important features of the various hypotheses.

We may summarise the more important experimental facts for the H_2—Cl_2 reaction as follows:—

(1) The reaction is initiated by light absorbed by the chlorine, and for mixtures hitherto employed the reaction rate is proportional to the light intensity. The upper limit of wave-length which is effective has not been established with certainty, but possibly may be as high as 590 $\mu\mu$.

(2) In presence of certain destructible impurities, notably ammonia and other nitrogeneous bodies, induction periods are obtained during which little or no combination of H_2 and Cl_2 takes place.

(3) The reaction is inhibited by oxygen, whose concentration suffers but little diminution during the experiment. The small amount thus disappearing is converted into H_2O by a chlorine-sensitised reaction.

(4) The reaction is characterised by a very high quantum yield. In mixtures comparatively free from oxygen and at atmospheric pressure, quantum yields of 10^5 may be obtained. With decreasing total pressure, however, the quantum yield diminishes a hundred- and even a thousand-fold on reducing the pressure to a fraction of a millimetre (Marshall).

(5) Agreement has not been reached in regard to the kinetics of the reaction. One or other of the equations given on p. 529 seems best to summarise our present knowledge of the dependence of reaction rate on the concentrations of H_2, Cl_2, and O_2.

(6) (*a*) Thorough desiccation (i.e. reduction of p_{H_2O} to 10^{-7} mm.) completely prevents reaction in visible light. (*b*) With somewhat greater concentrations of water vapour the reaction rate is a function

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* For a more complete discussion of reaction mechanism, see Thon's "Die Chlorknallgasreaktion"—*Fortschritte der Chemie, Physik und physikalischen Chemie*, **18**, Heft 11, 1926.

of p_{H_2O}. (*c*) At still higher partial pressures of H_2O the reaction velocity is independent of p_{H_2O}. The lower limit of p_{H_2O} in (*c*) is not exactly known; it may be as low as 10^{-4} or 10^{-5} mm. but probably is greater. (*d*) In ultra-violet light, reduction of the water content to $p_{H_2O} = 10^{-7}$ mm. does not completely prevent reaction; the quantum yield is, however, enormously reduced.

(7) The reaction has a temperature coefficient very little removed from unity (Porter, Bardwell, and Lind, *J. Amer. Chem. Soc.*, **48,** 2603, 1926).

(8) The photo-reaction and the radiochemical action (the combination under the influence of α-rays) are very similar. The ratio of the radiochemical yield to the quantum yield is a constant independent of the sensitivity of the mixture (cf. p. 430).

It is these facts—and in especial, their quantitative aspects—which must be taken into account by any theory of the reaction. Of chief importance for the discussion of reaction mechanism is the true kinetic law for the process ((5) above); unfortunately, however, agreement here has not been reached. In this connection it is pertinent to emphasise that (*a*) the reaction rate is so sensitive to traces of inhibitors that the determination of the true kinetic law by comparison of the velocities of combination in different experiments is a problem of some experimental difficulty, and (*b*) even if this law were known with certainty, it might not of itself be sufficient to enable a decision to be made between two widely different theories of reaction. Before dealing with these and other debatable points, let us first consider one feature of the reaction in regard to whose interpretation there appears to be general agreement. We refer to the high quantum yields, and there can be little doubt that to account for these one must assume a chain mechanism of some type. The characteristic feature of a chain mechanism is that either the primary light process itself or some subsequent stage of the reaction produces a body—the carrier of the chain—which can of itself react with, or render active, fresh reactant molecules. The carrier, when once formed, establishes a cycle of consecutive reactions, two results of which are (1) regeneration of the carrier and (2) the formation of the resultants of the change as by-products of the cycle. The chain is only ended—and correspondingly the quantum yield for the photo-reaction maintained finite—through the destruction of the carrier by processes other than those necessary to maintain the cycle. Naturally, when very large quantum yields are obtained in a chain reaction, the probability of such destruction of the carrier of the chain must be correspondingly small.

Apart from the obvious criterion that the reaction scheme postulated should furnish the net result of a kinetic law which is not incompatible with experience, any chain mechanism must conform to two general conditions. (1) Whether or not the carrier and other intermediate products of the cycle are chemically isolable substances—atoms, activated molecules, radicals, or unstable compounds may be concerned—the postulate of their occurrence under the experimental conditions must at least be plausible, and they must be such as could react with appropriate velocity in the manner specified by the reaction scheme. (2) For reactions like the H_2—Cl_2 reaction with very large quantum yields, it is impossible that one complete cycle initiated by a carrier molecule should regenerate more than a single carrier molecule. For example, if each cycle resulted in the production of *two* carrier molecules, we could obtain a large but finite quantum yield only if the chance of each carrier molecule repeating the cycle is very slightly less than one-half. Similarly, if *three* carrier molecules were generated per cycle, the chance of repeating the cycle would have to be assumed to be a fraction only slightly less than one-third. Such conditions as these are intrinsically very improbable, and it is much more likely that the cycle always regenerates the same amount of carrier as it uses up, the high quantum yield of the total process being then determined by the very small probability of an alternative non-regenerative reaction of the carrier. The choice of chain-reaction mechanism and the type of the intermediate processes which form the cycle of reactions naturally depend on the nature of the primary process which is the direct result of the act of absorption. The carriers of the chain are produced directly or indirectly from this primary process. In practically all theories of hydrogen-chlorine combination, such carriers are either atoms or activated molecules, and we may speak thus of " atom " chains or " activated " or " hot " molecule chains respectively. The mechanisms to be considered below all represent elaborations or modifications either of the Bodenstein " hot " molecule concept or of the Nernst atom chain. These two theories have already been briefly touched upon in this and in Chapter VIII., and, as mentioned, either of them gives a formal interpretation of the large quantum yields obtainable in the photo-reaction. We shall first discuss the application of the activated molecule theory to the kinetics of the reaction.

Activated Molecule Theories of the Reaction.—In 1916, Bodenstein (*Z. Elektrochem.*, **22,** 58, 1916) abandoned his previously suggested mechanism involving a photoelectric effect of light on the chlorine, and substituted a scheme represented † by the following :—

(2) $Cl_2 + h\nu + H_2 \rightarrow 2HCl^*$
(3) $HCl^* \rightarrow HCl$
(4) $HCl^* + O_2 \rightarrow HCl + O_2^*$
(5) $HCl^* + Cl_2 \rightarrow HCl + Cl_2^*$
(7) $Cl_2^* \rightarrow Cl_2$
(8) $Cl_2^* + H_2 \rightarrow 2HCl^*$.

The carriers of the chains are assumed to be activated HCl molecules, which, on collision, may energise fresh chlorine molecules (reaction 5). The chains may be destroyed by reactions (3) and (7) or by oxygen (reaction 4). It was suggested by Bodenstein that as a consequence of the last of these reactions, activated oxygen molecules are transformed into ozone, which again reverts to oxygen, whose concentration thus remains constant. From this mechanism he deduced the kinetic expression

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† The notation of Bodenstein is retained.

$$-\frac{d[H_2]}{dt}=\frac{k_2k_5I_0[Cl_2]^2}{k_3+k_4[O_2]} \quad . \quad . \quad . \quad . \quad (9)$$

In the derivation the following assumptions were made :—

(α) That the absorption of Cl_2 is weak, so that the light energy absorbed is proportional to $I_0[Cl_2]$. (It may be noted now that this assumption appears in the derivation of the kinetic expressions in *all* reaction mechanisms.)

(β) That the rate of reaction (2) is equal to $k_2I_0[Cl_2]$, i.e. is independent of $[H_2]$, which can only be true at sufficiently high hydrogen concentrations.

(γ) That reaction (7) may be neglected in comparison with (8).

Equation (9) is in agreement with the results of Bodenstein and Dux for the range $[H_2] > \frac{1}{4}[Cl_2]$, provided that k_3 may be neglected compared to k_4. However, it is not possible to obtain from the above mechanism, as it stands, either equation I or II (p. 529), one of which must be regarded, in the present state of our knowledge, as the " true " kinetic law of the process. Yet according to Thon (*Fortschritte der Chemie*, **18,** Heft 11, 1926) a slight modification of the Bodenstein mechanism permits the derivation therefrom of equation I. He divided the primary process (reaction (2)) into the two part-processes

(1) $Cl_2 + h\nu \rightarrow Cl_2{}^*$
(8) $Cl_2{}^* + H_2 \rightarrow 2HCl^*$.

Calculation then gives

$$\frac{dx}{dt}=\frac{k_1k_8I_0[H_2][Cl_2]\{k_3+k_4[O_2]\}+k_1k_5k_3I_0[H_2][Cl_2]^2}{\{k_7+k_8[H_2]\}\{k_3+k_4[O_2]\}+k_5k_7[Cl_2]}.$$

If now we neglect k_7 compared with $k_8[H_2]$ and put $k_3 = 0$, then

$$\frac{dx}{dt}=\frac{k_1k_8I_0[H_2][Cl_2]\{k_4[O_2]+k_5[Cl_2]\}}{k_4k_8[H_2][O_2]+k_5k_7[Cl_2]}.$$

This equation assumes the form of equation I if we may put

$$k_4[O_2] \ll k_5[Cl_2],$$

i.e. we obtain

$$\frac{dx}{dt}=\frac{k_1k_5k_8I_0[H_2][Cl_2]^2}{k_4k_8[H_2][O_2]+k_5k_7[Cl_2]} \quad . \quad . \quad . \quad (10)$$

(See, however, footnote, p. 547.)

Thon remarks : " The obtaining of this formula was made possible by writing Bodenstein's scheme as

(1) $Cl_2 + h\nu \rightarrow Cl_2{}^*$
(4) $HCl^* + O_2 \rightarrow HCl + O_2{}^*$
(5) $HCl^* + Cl_2 \rightarrow HCl + Cl_2{}^*$
(7) $Cl_2{}^* \rightarrow Cl_2$
(8) $Cl_2{}^* + H_2 \rightarrow 2HCl^*$.

"The scheme is distinguished by its simplicity. Its characteristics are:—

(*a*) The primarily formed HCl* leads to chains.
(*b*) The activated Cl_2^* molecule formed by collision of Cl_2 with HCl* is identical with that formed by light absorption.
(*c*) The same Cl_2^* reacts with H_2 forming HCl.* In the event of its not colliding with H_2 within its life period, it reverts to Cl_2. HCl* does not revert to HCl ($k_3 = 0$).
(*d*) Oxygen retardation is caused by collision of O_2 with HCl* molecules."

Admitting that the primary action of light on chlorine *may* be an activation and not a disruption, there are still two objections that may be urged against this theory of the reaction mechanism. The first is connected with the specific nature of energy transfer from activated HCl molecules. This energy transfer is supposed to take place only when the colliding molecule is either Cl_2 or O_2, but not when it is H_2 (or HCl). Although the assumption of similar specific transfers of energy has been introduced into the theory of thermal reactions (Christiansen and Kramers, *Z. physikal. Chem.*, **104**, 451, 1923), it may be still allowable to doubt whether the difference between the average result of collisions between HCl* and Cl_2 and that of collisions between HCl* and H_2 is as extreme as that postulated by the theory. The second objection is in respect of the assumption of reaction (8), that *two* activated particles result. We have seen (p. 545) that if this is the case, the quantum yield of the whole process could only remain finite by making unlikely assumptions regarding the relative probabilities of reactions (7) and (8).†

The latter objection is obviated in the reaction mechanism proposed by D. L. and M. C. C. Chapman (*J.C.S.*, **123**, 3079, 1923). Modifying previous views advanced by D. L. Chapman and his co-workers relative to the rôle of oxygen in the photo-combination, they suggest that active chlorine is deactivated not by oxygen

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† It might with justice be asked how it is that in equation (10), the kinetic expression deduced by Thon on the basis of this mechanism, the possibility of an infinite quantum yield is not apparent. It is, in fact, due to an error in the calculation—to neglect of the factor 2 in the resultant term (2HCl*) of process (8). Correct calculation gives, in place of equation (10), the expression

$$\frac{dx}{dt} = \frac{2k_1k_8I_0[H_2][Cl_2]^2}{k_4k_8[H_2][O_2] + k_5k_7[Cl_2] - k_5k_8[H_2][Cl_2]}.$$

It is clear from this that a real finite speed is obtained only when $k_5k_8[H_2][Cl_2] < k_4k_8[H_2][O_2] + k_5k_7[Cl_2]$. The assumption has already been made that $k_5[Cl_2] \gg k_4[O_2]$, i.e. that $k_5k_8[H_2][Cl_2] \gg k_4k_8[H_2][O_2]$, so that, in order to obtain a real velocity, the term $k_5k_7[Cl_2]$ must either be equal to or greater than $k_5k_8[H_2][Cl_2]$, i.e. $k_7 \geqq k_8[H_2]$. If a high quantum yield is to be obtained, this means that there must be about equal chances of a Cl_2^* molecule reacting according to (7) and according to (8), independently of the hydrogen concentration, an unlikely event. This objection to Thon's mechanism may be evaded by writing his equation (8) as (8′) $H_2 + Cl_2^* \rightarrow HCl^* + HCl$ or as equations (6) and (7) of Chapman's mechanism (p. 548).

alone but by the joint agency of oxygen and hydrogen. In mixtures containing chlorine and oxygen, it is supposed that, on illumination, the light energy absorbed by the former gas is shared between the chlorine and the oxygen, and a rapid reversible change given by the equation

$$Cl_2^* + O_2 \rightleftharpoons O_2^* + Cl_2$$

takes place. Degradation of energy of activation is assumed to occur in two ways: (1) by a spontaneous deactivation of Cl_2^* molecules, and (2) by collision of O_2^* molecules with H_2, with resulting water formation. No degradation of energy occurs in the actual H_2—Cl_2 reaction itself, i.e. an activated resultant particle is formed which inevitably transfers its excess energy to Cl_2 molecules. The complete scheme is represented by the equations

(1) $Cl_2 + h\nu \rightarrow Cl_2^*$
(2) $Cl_2^* + O_2 \rightarrow Cl_2 + O_2^*$
(3) $O_2^* + Cl_2 \rightarrow O_2 + Cl_2^*$
(4) $Cl_2^* \rightarrow Cl_2$
(5) $O_2^* + 2H_2 \rightarrow 2H_2O$
(6) $Cl_2^* + H_2 \rightarrow H_2Cl_2^*$
(7) $H_2Cl_2^* + Cl_2 \rightarrow 2HCl + Cl_2^*$.

It will be noticed that in reaction (6) only *one* molecule of an activated product ($H_2Cl_2^*$) is supposed to result. Calculation on the basis of this scheme leads to

$$\frac{d[HCl]}{dt} = \frac{2k_1k_3k_6I_0[H_2][Cl_2]^2}{k_2k_5[H_2]^2[O_2] + k_3k_4[Cl_2]} \qquad . \quad . \quad (11)$$

the only additional assumption introduced being that the term $k_5[H_2]^2$ may be neglected compared with $k_3[Cl_2]$. It will be observed that this equation is only slightly different from that suggested by M. C. C. Chapman as the best expression of her experimental results, the sole difference being in the term in the denominator containing $[H_2]^2$. In the empiric formula, the same term contains $[H_2]$ raised to a power in the neighbourhood of 1·6. In the derivation of equation (11) it was assumed that the rate of water formation is given by the mass-action expression $k_5[H_2]^2[O_2^*]$; this may, however, not be the case, for it could equally well be assumed that water formation is a complex process whose rate may be proportional to $[H_2]$ or to $[H_2]$ raised to some other power such as 1·5. Whatever exponent for $[H_2]$ is assumed for the rate of reaction (5), the same exponent of $[H_2]$ appears in the first term of the denominator in the final expression for the rate of HCl formation. The theory thus does not stand or fall by any particular value for this exponent.

Chapman's theory of the photo-combination is of considerable interest; it emphasises the view that oxygen retardation is due solely to water formation, and it accounts for the retardation by hydrogen (found by Chapman) in terms of an increased rate of water formation in presence of excess hydrogen. The two chief criticisms which may be levelled against the theory are

(*a*) the objection—common to all activated molecule theories—to the assumption that the activated resultant ($H_2Cl_2^*$ in this case) transfers its excess energy only to Cl_2 and not to other molecular species;

(*b*) that the rate of water formation deduced on the basis of this theory is in disagreement with that experimentally found either by Norrish and Rideal or by Cremer (cf. p. 531).

Another activated molecule theory, which need not be discussed here, has been suggested by Thon (*loc. cit.*, p. 48). It accepts the Chapman view that the primary stage in oxygen retardation is due to collisions of activated chlorine molecules with oxygen, but postulates two types of Cl_2^* molecules.

Atom Chain Theories.—Although the theory of activated molecule chains in the hydrogen-chlorine reaction may hardly yet be regarded as untenable, most investigators have preferred to employ and most discussion has centred round atomic chain mechanisms. As already pointed out, if dissociation of chlorine into atoms in one elementary act be accepted as the primary "light" process, some type of atomic chain theory almost necessarily follows, whereas secondary production of chlorine atoms may naturally still be postulated if one retains the view that the primary process is an activation of the chlorine molecule. Since the appearance of the first atom chain theory of Nernst, several such atom chain theories have been suggested, and certain questions of importance have in consequence arisen. Among these are (α) whether, in addition to chlorine atoms, hydrogen atoms are necessarily components of the chain; (β) whether, in view of the Franck theory of primary dissociation into a non-activated and an activated chlorine atom, any difference in chemical reactivity exists between these two; and (γ) the question of the rôle of water vapour in the chain mechanism.

The simplest atom chain theory was first suggested by Nernst in 1916 (*Z. Elektrochem.*, **22**, 62, 1916) and more fully developed in 1918 (*ibid.*, **24**, 335, 1918). The Nernst theory is expressed by the scheme

$$Cl_2 + h\nu \rightarrow 2Cl$$
$$Cl + H_2 \rightarrow HCl + H \quad . \quad . \quad . \quad (a)$$
$$H + Cl_2 \rightarrow HCl + Cl \quad . \quad . \quad . \quad (b)$$

Reactions (*a*) and (*b*) continue as a cycle, until they are ended by one or other of the reactions

$$H + H \rightarrow H_2 \quad . \quad . \quad . \quad . \quad . \quad (c)$$
$$Cl + Cl \rightarrow Cl_2 \quad . \quad . \quad . \quad . \quad . \quad (d)$$
and $$H + Cl \rightarrow HCl \quad . \quad . \quad . \quad . \quad . \quad (e)$$

In the presence of oxygen (or other inhibitor), however, in place of reactions (*c*), (*d*), and (*e*), the reactions ending the chain were assumed to be such processes as

$$H + O_2 \rightarrow HO_2 \quad \text{and} \quad Cl + O_2 \rightarrow ClO_2,$$

the concentration of oxygen remaining constant by the occurrence of such reactions as

$$ClO_2 + Cl \rightarrow Cl_2 + O_2 \quad \text{and} \quad HO_2 + H \rightarrow H_2 + O_2.$$

Nernst calculated, on the basis of his Heat Theorem, that both reactions (*a*) and (*b*) are thermodynamically possible. For this he employed the old value of 106,000 cal. for the heat of dissociation of chlorine; using the more recent figure ($D_{Cl_2} = 57{,}700$ cal.), the conclusion is not so certain. Thus, assuming the heat of dissociation of hydrogen to be 100,000 cal., we obtain

$$Cl + H_2 \rightarrow HCl + H + 850 \text{ cal.} \qquad . \quad . \quad (a)$$
$$H + Cl_2 \rightarrow HCl + Cl + 43{,}150 \text{ cal.} \qquad . \quad . \quad (b)$$

and with higher values for D_{H_2} reaction (*a*) may even be slightly endothermic. But even if it be (thermodynamically) slightly endothermic, it cannot be ruled out as a link in the chain. It is to be remembered that the chlorine atoms formed in (*b*) will possess some part of the heat of reaction, either as energy of translation or as internal energy, and reaction (*a*) may thus be made possible and sufficiently so to "work" a chain.

The first attempt to derive an expression for the velocity of photocombination of hydrogen and chlorine from the Nernst theory was made in an interesting paper by Göhring (*Z. Elektrochem.*, **27,** 511, 1921), who also advanced a modified theory in which hydrogen atoms did not function. Assuming the preliminary formation of chlorine atoms, Göhring considered the various reaction possibilities in mixtures of H_2, Cl_2, and O_2. From a long list of such processes, he eliminated many as non-essential to the correct derivation of the kinetic expression. In effecting this he employed certain criteria, the chief of which were:

(*a*) All processes in which both reactants are atoms or molecules of short life-period (such as Cl_3) may be neglected, owing to the extremely small concentrations of the reacting substances.

(*b*) It is not necessary specifically to take into account such reactions as $ClO_2 + Cl \rightarrow Cl_2 + O_2$ and $HO_2 + H \rightarrow H_2 + O_2$, since it is assumed that the velocity constants of such processes are approximately the same as those of the reactions between O_2 and the active substances (H, Cl, Cl_3).

(*c*) Certain other assumptions in regard to relative speeds of reaction. As a result of elimination in this way, eight reactions were left (in addition to the primary process) for incorporation into a reaction scheme:—

$Cl_2 + h\nu \rightarrow 2Cl$	k
$Cl + Cl_2 \rightarrow Cl_3$	k_1
$Cl + H_2 \rightarrow HCl + H$	k_2
$Cl_3 + Cl_2 \rightarrow 2Cl_2 + Cl$	k_3
$Cl_3 + H_2 \rightarrow 2HCl + Cl$	k_4
$H + Cl_2 \rightarrow HCl + Cl$	k_5
$Cl + O_2 \rightarrow ClO_2$	k_9
$Cl_3 + O_2 \rightarrow ClO_2 + Cl_2$	k_{10}
$H + O_2 \rightarrow HO_2$	k_{11}

(Note that $[O_2]$ is maintained constant by such reactions as $Cl + ClO_2 \rightarrow Cl_2 + O_2$, $Cl + HO_2 \rightarrow HCl + O_2$, etc.; these reactions need not be considered further, however, in virtue of criterion (*b*).)

Göhring showed that, taking with the primary process reactions (2), (5), (9), and (11), one may derive the equation

$$+\frac{d[HCl]}{dt} = \frac{4kk_2k_5[Cl_2]^2[H_2] + 2kk_2k_{11}[Cl_2][H_2][O_2]}{k_5k_9[Cl_2][O_2] + k_2k_{11}[H_2][O_2] + k_9k_{11}[O_2]^2}.$$

Since we are dealing with mixtures in which $[O_2]$ is much less than $[H_2]$ or $[Cl_2]$, and since, according to Göhring, it is probable that the exothermic process (5) takes place at practically every collision between H and Cl_2 so that k_{11} cannot be much greater than k_5, the second term of the numerator may be neglected in comparison with the first. Also, Göhring postulates that k_9 cannot be much greater than k_2, so that the last term of the denominator may be neglected compared with the second. He thus obtains

$$+\frac{d[HCl]}{dt} = \frac{4kk_2k_5[Cl_2]^2[H_2]}{\{k_5k_9[Cl_2] + k_2k_{11}[H_2]\}[O_2]} \quad . \quad . \quad (12)$$

identical with our equation II of p. 529, one of the two best expressions of the experimental data on the kinetics of the reaction.

Göhring also obtained an equation of exactly similar type by combination of reactions (1), (4), (9), and (10) with the primary process. Thus, he derived the expression

$$\frac{d[HCl]}{dt} = \frac{4kk_1k_4[Cl_2]^2[H_2]}{k_1k_{10}[Cl_2][O_2] + k_4k_9[H_2][O_2] + k_9k_{10}[O_2]^2}.$$

Neglecting the term containing $[O_2]^2$, one obtains

$$\frac{d[HCl]}{dt} = \frac{4kk_1k_4[Cl_2]^2[H_2]}{\{k_1k_{10}[Cl_2] + k_4k_9[H_2]\}[O_2]} \quad . \quad . \quad (13)$$

Before discussing other atom chain theories and also theories of the rôle of water vapour in atomic chains, it is convenient first to deal with the criticisms which have been advanced against the Nernst-Göhring mechanism. A large number of such criticisms have been put forward by Marshall (*J. Physical Chem.*, **29,** 842, 1925) and by Thon—some of which apply only to the first Göhring mechanism in which hydrogen atoms appear, others, however, applicable to either chain theory.

Thon (*Fortschritte der Chemie*, **18,** Heft 11, 1926) shows that the following are among the consequences of an atom chain theory :—

(*a*) With sufficiently low oxygen concentrations, the kinetic equation for the reaction course must be one containing square roots of the concentration terms. This follows from the fact that if a finite velocity is to be obtained (in absence of oxygen), the chains must be ended, and this can occur only by reactions between atoms. Thus, if we assume a mechanism

$$\begin{array}{ll} Cl_2 + h\nu \rightarrow 2Cl \quad . \quad . \quad . \quad . \quad . & k \\ Cl + H_2 \rightarrow HCl + H \quad . \quad . \quad . \quad . & k_2 \\ H + Cl_2 \rightarrow HCl + Cl \quad . \quad . \quad . \quad . & k_5 \\ Cl + Cl \rightarrow Cl_2 \quad . \quad . \quad . \quad . \quad . & k_{13} \end{array}$$

we obtain

$$\frac{d[HCl]}{dt} = 2k_2\sqrt{\frac{kI_0}{k_{13}}} \cdot [Cl_2]^{\frac{1}{2}}[H_2] \quad . \quad . \quad . \quad (14)$$

If instead of $Cl + Cl \rightarrow Cl_2$ we substitute

$$H + H \rightarrow H_2 \, . \quad . \quad . \quad . \quad . \quad . \quad k_{20}$$

we find

$$\frac{d[HCl]}{dt} = 2kI_0[Cl_2] + 2k_5\sqrt{\frac{kI_0}{k_{20}}} \cdot [Cl_2]^{\frac{3}{2}},$$

in which the first term may be neglected compared to the second. If finally, in place of $Cl + Cl \rightarrow Cl_2$, we substitute

$$H + Cl \rightarrow HCl \quad . \quad . \quad . \quad . \quad . \quad k_{15}$$

a complicated expression containing square root terms is obtained for the reaction velocity.

(*b*) The presence of oxygen alters the form of the dependence of the reaction velocity on light intensity. In absence of oxygen the velocity should be proportional to $\sqrt{I_0}$ (cf. equation (14)), and perhaps some indication of deviation from proportionality between dx/dt and I_0 ought to be observable with low oxygen concentrations.

(*c*) Retardation by oxygen ought still to be present even at the lowest concentrations of hydrogen. This may be seen from equations (12) and (13) based on the Göhring mechanism, in both of which the velocity is inversely proportional to $[O_2]$.

With (*c*) Thon's own experimental work on the reaction is in agreement, Mrs. Chapman's, however, is not. With regard to (*a*) and (*b*), there are little or no experimental observations in support of either. Berthoud (*Helv. Chim. Acta*, **7,** 324, 1924) has indeed suggested that certain of Mrs. Chapman's results for mixtures containing low concentrations of H_2 are well reproduced by the equation $\frac{dx}{dt} = k[Cl_2][H^2]^{\frac{1}{2}}$, but this conclusion is probably unjustified. Further, though Mrs.

Chapman found that the reaction rate is proportional to a power of the light intensity slightly less than unity, the difference is hardly significant and practically within the experimental error. Further experimental work on the reaction in the presence of very low oxygen concentrations is necessary to test adequately these predictions of an atom chain theory of the reaction.

Among the objections raised by Thon to the theory of atomic chains, those relating to the mechanism of oxygen retardation appear to be of chief importance. According to Göhring, inhibition by O_2 takes place *via* processes (9), (10), and (11), and subsequent regeneration of O_2 by reactions such as

$$\left\{\begin{matrix} ClO_2 \\ HO_2 \end{matrix}\right\} + \left\{\begin{matrix} H \\ Cl \end{matrix}\right\} \rightarrow \left\{\begin{matrix} Cl_2 \\ H_2 \\ HCl \end{matrix}\right\} + O_2.$$

Yet, as Thon points out, oxygen has no effect on the rate of phosgene formation in the dark, a reaction which is almost certainly an atom reaction (Christiansen, *Inaugural Dissertation*, Copenhagen, 1921; Bodenstein and Plaut, *Z. physikal. Chem.*, **110,** 399, 1924) and which, according to Göhring, should be strongly retarded by oxygen. This objection applies to both of Göhring's mechanisms; others may be advanced against the mechanism in which the appearance of hydrogen atoms is postulated. For example, the combination of hydrogen and bromine is not retarded by oxygen, either in the dark or in light, yet the evidence is overwhelmingly in favour of the view that both hydrogen atoms and bromine atoms are involved in the process. It ought therefore—if the first Göhring mechanism applies—to be retarded by the reactions $H + O_2 \rightarrow HO_2$, $HO_2 + H \rightarrow H_2 + O_2$.

Again, hydrogen atoms react rapidly with HCl—most probably according to $HCl + H \rightarrow H_2 + Cl$; $H + Cl \rightarrow HCl$ (Bonhoeffer and Boehm, *Z. physikal. Chem.*, **119,** 385, 1926)—and the photochemical union of hydrogen and chlorine should thus be retarded by HCl.† Bonhoeffer and Boehm also find that H_2O_2 is one of the chief products of reaction between hydrogen atoms and oxygen; one must therefore

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† These two objections to the Nernst theory—(*a*) that derived from the non-retardation of the hydrogen-bromine reaction by oxygen, and (*b*) that relating to the non-retardation of the hydrogen-chlorine reaction by HCl—have been recently discussed by Bogdandy and Polanyi (*Z. Elektrochem.*, **33,** 554, 1927). They attempt to show that neither objection is sustainable; in our view, they are right in respect of (*a*) but not of (*b*). The absence of oxygen retardation in the H_2—Br_2 reaction is due, as these authors point out, to the fact that this process is not a chain reaction. Here, no chain follows the reaction

$$H + Br_2 \rightarrow HBr + Br;$$

the H atom is not regenerated. O_2 could retard this process only by collisions between H and O_2, and these would only be expected to be frequent at high oxygen concentrations, for which case no observations have been made.

Bogdandy and Polanyi also try to reconcile failure to detect retardation of the hydrogen-chlorine reaction by HCl with the Nernst mechanism, but we cannot agree with their treatment. It appears sufficient answer to their presume that after the first Göhring reaction $H + O_2 \rightarrow HO_2$, one or other of the secondary reactions $HO_2 + H_2 \rightarrow H_2O_2 + H$ or $HO_2 + H \rightarrow H_2O_2$ takes place to a marked extent. In this connection, it is necessary to note that the Nernst-Göhring theory makes no provision for water formation in the photo-union of hydrogen and chlorine. If, despite the above evidence against the appearance of hydrogen atoms in the reaction, the first Göhring mechanism be accepted, one might presume that water formation ensues from the H_2O_2 formed in the manner just postulated. On the other hand, with the second Göhring mechanism, which, on the whole, appears the less open to attack, one must assume some reaction between ClO_2 and H_2 in order to account for water formation. In absence of published attempts to extend the Nernst chain theory to account for water formation, we need not, however, speculate further in this direction.

Marshall (*J. Physical Chem.*, **29**, 842, 1925) tested the Nernst chain theory in the following manner. Hydrogen atoms, prepared by Wood's method, were led into chlorine and the extent of hydrochloric acid formation determined. The rate of supply of hydrogen atoms was estimated by similar experiments in which the hydrogen stream was passed into bromine and the resulting HBr determined, the assumption being made that one HBr molecule results from each hydrogen atom. It was found that the yield of hydrochloric acid per hydrogen atom increased with increasing pressure of the gas mixture, the values varying from about 7 at 6·0 mm. total pressure to 1 at 0·04 mm. Ammonia was, however, present in the reacting gases and this probably accounts for the low yield, but Marshall regards the variation of yield with pressure as significant. He rejects the Nernst mechanism in explanation of his results and prefers one in which activated molecules function, as given by the equations

$$\begin{aligned} &H + Cl_2 \rightarrow HCl^* + Cl \\ &HCl^* + Cl_2 \rightarrow Cl_2^* + HCl \\ &Cl_2^* + H_2 \rightarrow 2HCl^* \\ &Cl + Cl \rightarrow Cl_2. \end{aligned}$$

In view of the considerable amounts of inhibiting impurities present in these experiments, however, it is not possible to draw therefrom

views to point out that while a mechanism (1) $Cl_2 + h\nu \rightarrow 2Cl$, (2) $Cl + H_2 \rightarrow HCl + H$, (3) $H + Cl_2 \rightarrow HCl + Cl$, (4) $Cl + O_2 \rightarrow ClO_2$ yields for the velocity

$$\frac{d[HCl]}{dt} = \frac{4k_1k_2I_0[H_2][Cl_2]}{k_4[O_2]},$$

addition of reaction (5) $H + HCl \rightarrow H_2 + Cl$ to this scheme gives

$$\frac{d[HCl]}{dt} = \frac{4k_1k_2I_0[H_2][Cl_2]}{k_4[O_2]} \cdot \frac{1}{1 + \frac{k_5[HCl]}{k_3[Cl_2]}}.$$

HCl (either added or formed in the reaction) should thus affect the reaction velocity, if k_5 is of the same order as magnitude as k_3.

any conclusion adverse to the Nernst mechanism. Marshall's results might still be accounted for on the basis of the Nernst theory, if at low pressures relatively more inhibitor was present than at higher pressures.

We have seen that on passing hydrogen atoms into chlorine, hydrochloric acid is formed; but no detectable amount of HCl results when pre-illuminated chlorine, in which consequently there *might* be chlorine atoms, is led into hydrogen. On the other hand, considerable yields of HCl are obtained when chlorine atoms are liberated by chemical reaction *in presence of* hydrogen. This result has been regarded as favouring the Nernst chain theory, though it may equally well be interpreted in terms of any atom chain. Bogdandy and Polanyi (*Naturwiss.*, **18,** 410, 1927) passed into a hydrogen-chlorine mixture (5 mm. $H_2 + 0{\cdot}1$ mm. Cl_2) a stream of hydrogen containing Na vapour at a partial pressure of $\frac{1}{10000} - \frac{1}{1000}$ mm. They found that hydrochloric acid formation took place, the extent of which was always greater (up to 200 times) than the amount of NaCl formation. Hydrogen containing no sodium vapour does not combine with chlorine at the temperature employed (180°-240° C.). Further, the primary NaCl formation was so small that the heating of the gases which it caused could amount only to a few degrees, and the heating caused by the HCl formation itself was shown to be of no significance. The authors' interpretation of their results is that after the primary process

$$Na + Cl_2 \rightarrow NaCl + Cl,$$

the resultant chlorine atoms start a chain process in which HCl is formed. The latter is presumed to be the Nernst chain

$$\begin{gathered} Cl + H_2 \rightarrow HCl + H \\ H + Cl_2 \rightarrow HCl + Cl. \end{gathered}$$

It is of interest that the length of the chain (about 100 links) agrees well with that determined by Marshall (*J. Physical Chem.*, **29,** 1453, 1925) in the photochemical reaction at a pressure of a few millimetres. While these experiments are most plausibly interpreted in terms of atom chains, naturally all they show is that the energy-rich products of the reaction between Na and Cl_2 are able to initiate a chain reaction in hydrogen-chlorine mixtures.

Other types of atom chain theories have been recently advanced by Cremer (*Z. physikal. Chem.*, **128,** 285, 1927). Accepting the view of Franck, Kuhn, and others that chlorine is dissociated optically into an excited and a non-excited atom, he assumes that only the excited (Cl^*) atom takes part in the reaction, thereby avoiding certain of the objections raised by Thon and Marshall to other atom mechanisms. One of Cremer's reaction schemes is represented by

(1) $Cl_2 + h\nu \rightarrow Cl^* + Cl$
(2) $Cl^* + Cl_2 \rightarrow Cl_3^*$
(3) $Cl_3^* + H_2 \rightarrow 2HCl + Cl^*$
(4) $Cl^* + O_2 \rightarrow O_2^* + Cl$
(5) $Cl_3^* + O_2 \rightarrow O_2^* + Cl_2 + Cl$
(6) $Cl_3^* \rightarrow Cl_2 + Cl$
(7) $O_2^* + 2H_2 \rightarrow 2H_2O$
(9) $Cl^* \rightarrow Cl.$

Its characteristics are:

(*a*) Two hypothetical intermediate bodies leading to HCl formation are assumed. These are Cl^* and Cl_3^*. Reactions (2) and (3) constitute the chain.

(*b*) The intermediate body leading to water formation is assumed to be O_2^* and is formed by reactions (4) and (5). All O_2^* molecules produced are converted into water.

(*c*) In absence of O_2 the chains may be broken by (6) and (9).

It cannot be said that the scheme is inherently very plausible. The Cl atom is assumed to be non-reactive, but an activation to the extent of but 2500 cal. per gram-atom is presumed to effect the required gain in reactivity. Again, reaction (4) is not easily justified, and even assuming the transference of the small energy of activation of Cl^* to O_2 molecules to take place, it is hardly likely that the O_2^* thus formed could be reactive enough to combine with hydrogen. Cremer suggests, as alternative to processes (4), (5), and (7), the formation of unstable intermediate products ($Cl^*. . . O_2$) and ($Cl_3^* . . . O_2$), which react with hydrogen to form water.

Although Cremer's scheme, in which definite intermediate products are postulated, is open to criticism, nevertheless there are indications that it is of the right general type, and that if we label the unknown intermediate substances A, B, and C, the correct reaction scheme is that illustrated in Fig. 49. Here A is the product formed by light absorption (Cl^* in the special scheme above given), B is the intermediate product leading to water formation, and C the product leading to the formation of HCl. The arrows show the directions in which reaction occurs, and make clear how the chain is kept intact by reactions (2) and (3) and broken by processes (9), (4), (5), and (6). This reaction mechanism is of considerable interest and we must deal —though as briefly as possible—with certain of its implications.

Cremer (*loc. cit.*) shows that the kinetic expressions for hydrochloric acid formation found by various authors may be simply derived on the basis of this scheme, that it suggests an explanation of the discrepant results of Thon and of Chapman and others, and that it is not incompatible with experimentally determined values of the quantum yield and of the ratio HCl formed/H_2O formed in H_2—Cl_2—O_2 mixtures. Taking all eight equations simultaneously into account yields a very complicated kinetic expression, but according to Cremer this is unnecessary, since we may distinguish between processes (1), (2), (3), and

(4) as principal processes and (5), (6), and (9), as subsidiary processes. Taking into consideration only the principal processes, one obtains directly the Bodenstein-Dux expression

$$\frac{d[2\mathrm{HCl}]}{dt}=\frac{k_1k_2I_0[\mathrm{Cl}_2]^2}{k_4[\mathrm{O}_2]}$$

for the rate of HCl formation. The subsidiary processes (5), (6), and (9) play only a secondary part and, except under extreme conditions, affect the kinetic expression only by necessitating the introduction of minor correction terms. Cremer deals with three cases in which one or other of these subsidiary process exerts an influence, all of which cases he suggests have been experimentally realised. These are:—

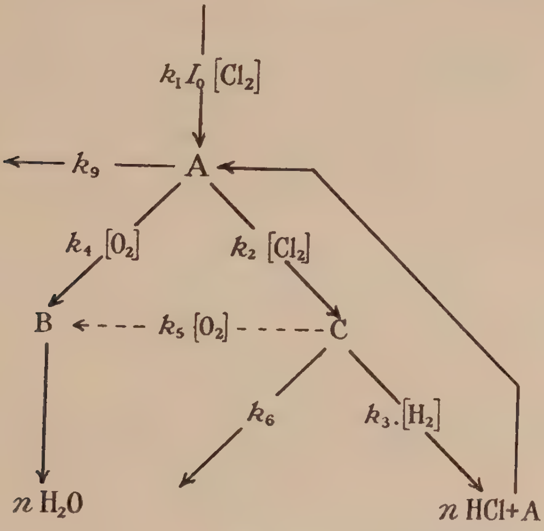

FIG. 49.

(α) Reactions (5) and (9) may be disregarded compared with (6). (Experiments of Chapman and of Cremer.)

(β) Reactions (6) and (9) may be neglected compared with (5). (Experiments of Thon with $p_{\mathrm{O}_2} > 0{\cdot}2$ mm.)

(γ) Only reaction (6) may be neglected. (Experiments of Thon with $p_{\mathrm{O}_2} < 0{\cdot}2$ mm.)

In the first case, (6) $\mathrm{Cl_3}^* \rightarrow \mathrm{Cl}_2 + \mathrm{Cl}$ is the important subsidiary process. Using processes (1), (2), (3), (4), and (6) we obtain

$$\frac{d[2\mathrm{HCl}]}{dt}=\frac{k_1k_2k_3I_0[\mathrm{Cl}_2]^2[\mathrm{H}_2]}{k_2k_6[\mathrm{Cl}_2]+k_3k_4[\mathrm{H}_2][\mathrm{O}_2]+k_4k_6[\mathrm{O}_2]} \quad . \quad (15)$$

It may be shown that $k_4k_6[O_2]$ is to be neglected compared with $k_2k_6[Cl_2]$.† The equation is then formally identical with that obtained experimentally by Cremer, and not very different from that found by Mrs. Chapman. The former obtained

$$\frac{d[2HCl]}{dt} = k_C \frac{[Cl_2]^2[H_2]}{[Cl_2] + 0{\cdot}02[H_2][O_2]} \quad . \quad . \quad . \quad (8)$$

Comparison of equations (15) and (8) gives

$$\frac{k_3k_4}{k_2k_6} = 0{\cdot}02 \quad . \quad . \quad . \quad . \quad (16)$$

Starting with this equation, it is possible to gain an idea of the relative magnitudes of the individual constants in equation (15) and to predict the quantum yield in mixtures of known H_2, Cl_2, and O_2 contents. Considering Fig. 49 and remembering that processes (5) and (9) are excluded, it is seen that the intermediate substance A either reacts with Cl_2 to form C or with O_2 to form B (which eventually goes to H_2O), and that C either reacts with H_2 re-forming A or spontaneously loses its activity according to (6). The probability that A reacts with Cl_2 is thus

$$w_2 = \frac{k_2[Cl_2]}{k_4[O_2] + k_2[Cl_2]},$$

the probability that it reacts with O_2 (eventually yielding H_2O) is

$$w_4 = \frac{k_4[O_2]}{k_4[O_2] + k_2[Cl_2]}.$$

Similarly, the probability that C spontaneously loses its activity is

$$w_6 = \frac{k_6}{k_6 + k_3[H_2]},$$

and the probability that it reacts with H_2 to form HCl + A is

$$w_3 = \frac{k_3[H_2]}{k_6 + k_3[H_2]}.$$

If we can determine the ratios $\frac{k_2}{k_4} = a$ and $\frac{k_3}{k_6} = b$, the quantum yield of the process may be predicted. Equation (16) forms one relation between the constants k_2, k_3, k_4, and k_6; another is obtained from experimentally determined values of the ratio $\frac{\text{HCl formed}}{\text{H}_2\text{O formed}}$. Evidently the latter is given by the probability ratio

$$\frac{w_2w_3}{w_4} = \frac{k_2k_3[Cl_2][H_2]}{k_4[O_2]\{k_3[H_2] + k_6\}},$$

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† See page 559 where it is shown that $\frac{k_2}{k_4} = 23$.

and k_6 may be neglected compared with $k_3[H_2]$,† so that we obtain

$$\frac{\text{HCl formed}}{\text{H}_2\text{O formed}} = \frac{\frac{k_2}{k_4}\cdot[Cl_2]}{[O_2]} = a\cdot\frac{[Cl_2]}{[O_2]}.$$

By application of this equation to his experimental data, Cremer finds a mean value for a of 23, consequently $b = 0{\cdot}46$,

i.e. $$\frac{k_2}{k_4} = 23 \text{ and } \frac{k_3}{k_6} = 0{\cdot}46.$$

In one of his experiments, $[H_2] = 200$ (expressed in mm.) and $[Cl_2] = [O_2] = 150$. Consequently,

$$\frac{w_2}{w_4} = \frac{k_2}{k_4} = a = 23\,;\;\; w_2 + w_4 = 1\,;\;\; w_2 = \frac{23}{24},\;\; w_4 = \frac{1}{24};$$

and $$\frac{w_3}{w_6} = \frac{k_3[H_2]}{k_6} = b[H_2]\,;\;\; w_3 + w_6 = 1\,;$$

hence

$$\frac{w_3}{w_6} = 92\,;\;\; w_3 = \frac{92}{93},\;\; w_6 = \frac{1}{93};$$

Now w_2w_3 is the probability that the chain continues, $1 - w_2w_3$ is the probability that it breaks. Consequently the mean length of the chain is

$$x = \frac{w_2w_3}{1 - w_2w_3} = 18.$$

Since each link in the chain produces two HCl molecules, the quantum yield predicted is 36, which agrees very well with that experimentally obtained in this particular experiment.

The second case to be treated is when (5) is the important subsidiary process, (6) and (9) being neglected. From equations (1), (2), (3), (4), and (5) one finds

$$\frac{d[2HCl]}{dt} = \frac{k_1k_2k_3I_0[Cl_2]^2[H_2]}{[O_2]\{k_2k_5[Cl_2] + k_3k_4[H_2]\}},$$

a term $k_4k_5[O_2]$ having been neglected, owing to the smallness of $k_4[O_2]$ compared with $k_2[Cl_2]$. This equation agrees formally with that obtained experimentally by Thon, viz.

$$\frac{d[2HCl]}{dt} = \frac{k[Cl_2]^2[H_2]}{[O_2]\{[H_2] + 0{\cdot}1[Cl_2]\}}.$$

Thon's experiments were carried out in a clean dry quartz apparatus, while Mrs. Chapman used a modification of the Bunsen actinometer whose glass walls were moist, and Cremer used a glass apparatus containing P_2O_5 which, it is suggested, was covered with a damp layer from the water resulting from the reaction. Cremer considers that Thon's results differ from his own and Chapman's owing to different catalytic effects of the walls on one of the part-processes of the total reaction. The process (6) $Cl_3^* \rightarrow Cl_2 + Cl$ is suggested as the reaction concerned; under Thon's experimental conditions $k_6 = 0$, while in Chapman's and Cremer's reaction vessels k_6 is of greater importance than k_5.

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† Otherwise a high quantum yield would not be obtained when the concentration of O_2 is small.

There is nothing implausible in the theory that a wall-effect exerts an influence on the photo-union of hydrogen and chlorine, and indeed the same suggestion has been made by other investigators; we have, however, no means of judging the degree of plausibility of the special hypothesis here advanced that Cl_3^* is deactivated only on collision with a surface. Cremer thus considers that the "true" kinetic expression for HCl formation in the light is

$$\frac{d[2\text{HCl}]}{dt} = \frac{k[\text{Cl}_2]^2][\text{H}_2]}{[\text{O}_2]\{[\text{Cl}_2] + k''[\text{H}_2]\}},$$

but that, owing to catalytic influences of the material of the surface of the reaction vessel, the law

$$\frac{d[2\text{HCl}]}{dt} = \frac{k[\text{Cl}_2]^2[\text{H}_2]}{[\text{Cl}_2] + k'[\text{H}_2][\text{O}_2]}$$

may be obeyed.

The third case, in which reaction (9) is introduced together with (5), arises from the question as to the manner in which the chains end when $[O_2] = 0$. If one assumes that k_6 is never quite zero (under Thon's experimental conditions), one obtains, as may be seen by placing $[O_2] = 0$ in equation (15), the limiting expression

$$\frac{d[2\text{HCl}]}{dt} = k[\text{H}_2][\text{Cl}_2]$$

for zero oxygen content. There is, however, in Thon's experiments with lowest oxygen concentrations, no indication of any tendency towards such a limiting expression; in all cases the $[Cl_2]^2$ law was confirmed. It is then found necessary, in order to preserve the latter for the limit of zero oxygen concentration, to assume the occurrence of a spontaneous deactivation of the intermediate body A, i.e. in the specialised scheme to postulate the reaction

$$(9)\ \text{Cl}^* \rightarrow \text{Cl}.$$

This reaction will be of significance only in mixtures of low oxygen content, and Cremer shows that its introduction into the scheme leads to consequences which are not in disagreement with Thon's experimental results for mixtures containing low partial pressures of oxygen ($p_{O_2} <$

0·2 mm.). Cremer attempts to obtain an estimate of the value of k_9 by calculation from Thon's experiments; he finds that $\frac{k_9}{k_4} = 0{\cdot}0023$, but as the basis of the calculation is somewhat uncertain, we need not here reproduce the methods employed. It is of interest, however, to note that from this estimate of k_9 one may deduce the *greatest possible* quantum yield for the reaction (i.e. the yield in complete absence of oxygen). It is calculated that for a stoichiometric mixture of H_2 and Cl_2 at one atmosphere pressure, the maximum yield is 7·6 . 10^6 HCl molecules per quantum. (The highest value obtained experimentally is 1·1 . 10^5 (Kornfeld and Müller, *Z. physikal. Chem.*, **117**, 242, 1925).)

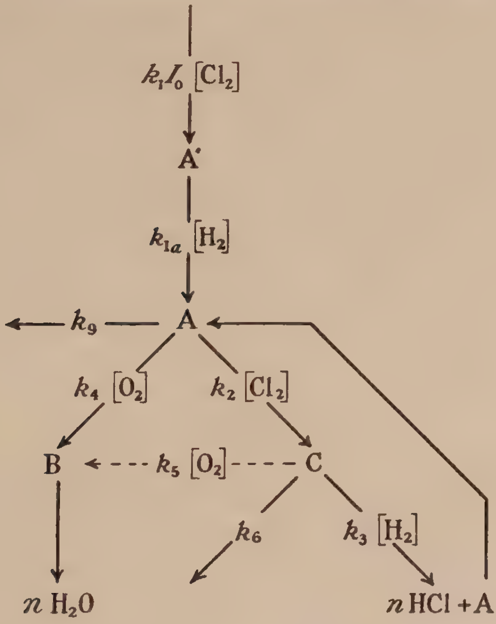

FIG. 50.

The specialised scheme given on p. 556 with the active intermediate products Cl^* and Cl_3^* is not the only one from which the kinetic expressions I and II of p. 529 may be derived. Cremer suggests, for example, an alternative formulation represented by

(1) $Cl_2 + h\nu \rightarrow Cl^* + Cl$
(1*a*) $Cl^* + H_2 \rightarrow HCl^* + H$
(2) $HCl^* + Cl_2 \rightarrow HCl + Cl_2^*$
(3) $Cl_2^* + H_2 \rightarrow HCl + HCl^*$
(4) $HCl^* + O_2 \rightarrow HCl + O_2^*$
(6) $Cl_2^* \rightarrow Cl_2$,

with which, if we add

(5) $Cl_2^* + O_2 \rightarrow Cl_2 + O_2^*$
(7) $O_2^* + 2H_2 \rightarrow 2H_2O$
and (9) $HCl^* \rightarrow HCl$,

we obtain the scheme illustrated by the diagram of Fig. 50.

Comparison of this with Fig. 49 shows that essentially they are identical. No doubt other reaction schemes with different hypothetical intermediate bodies could be set up leading to the same formulation of the reaction kinetics.

Theories of Sensitised Water Formation in the Hydrogen-Chlorine Reaction.—The various theories of sensitised water formation have already been stated and to some extent discussed in previous sections of this Chapter, but there yet remains for brief discussion the kinetics of the process. If the possibility of the occurrence of a direct or chlorine-sensitised reaction between HCl and O_2 be disregarded, all theories of sensitised water formation postulate that H_2 is one of the reactants, the other being activated oxygen or an oxygen-containing compound. It will be recalled that, according to Norrish and Rideal, the rate of water formation in H_2—Cl_2—O_2 mixtures on illumination with light of constant intensity is given by

$$+\frac{d[H_2O]}{dt} = k[Cl_2][O_2] \quad . \quad . \quad . \quad (17)$$

whereas Cremer finds

$$+\frac{d[H_2O]}{dt} = k[Cl_2] \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Without attempting a decision between the two, it may be noted that it is very difficult if not impossible to derive equation (17) theoretically on the basis of any mechanism which simultaneously and with the same assumptions yields the correct result for the rate of HCl formation; on the other hand, equation (18) is derivable without special trouble on the basis either of an " atom " mechanism or of an activated molecule theory. Rideal and Norrish (*J.C.S.*, **127,** 790, 1925) derive equation (17) from the following reaction scheme :—

(*a*) $Cl_2 + h\nu \rightarrow Cl_2^*$
(1) $Cl_2^* \rightarrow Cl_2$
(2) $Cl_2^* + O_2 \rightarrow Cl_2 + O^e$
(3) $Cl_2^* + H_2 \rightarrow 2HCl$
(4) $Cl_2^* + Cl_2 \rightarrow Cl_2 + 2Cl$ (followed by the Nernst chain)
(5) $O^e \rightarrow O_2$
(6) $O^e + H_2 \rightarrow H_2O$.

Here O^e denotes an activated oxygen molecule.

From these equations one obtains

$$+\frac{d[H_2O]}{dt} = \frac{k_a k_2 k_6 I_0 [Cl_2][O_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \cdot \frac{[H_2]}{k_5 + k_6[H_2]},$$

which reduces to

$$+\frac{d[H_2O]}{dt}=\frac{k_a k_2 I_0}{k_1}\cdot[Cl_2][O_2],$$

if the assumptions be made that

(α) k_1 is large compared with $k_2[O_2]$, $k_3[H_2]$, and $k_4[Cl_2]$;
(β) k_5 may be neglected in comparison with $k_6[H_2]$.

The first assumption has been criticised by Thon (*Fortschritte*, **18,** Heft 11, 56), and indeed it does differ radically from pre-conceived ideas on the subject. It is to be noted that according to Norrish and Rideal's theory, water formation has nothing to do with oxygen retardation, for the latter is supposed to occur in an unspecified manner by intervention of oxygen in the chain mechanism of HCl formation. The assumption that k_1 is large compared with $k_4[Cl_2]$ naturally means that only a small fraction of the optically excited molecules succeed in starting chains, and hence that the true length of the chain is much greater than the experimentally determined quantum efficiency. While there may be insufficient grounds for rejecting these views, they will hardly be acceptable until it is shown that the same assumptions lead to a velocity of HCl formation not incompatible with experiment. With regard to other activated molecule theories of the reaction, it may be shown that Chapman's theory (cf. p. 548) gives for the velocity of water formation in H_2—Cl_2—O_2 mixtures

$$\frac{d[H_2O]}{dt}=\frac{kI_0[H_2]^2[O_2]}{k'[H_2]^2[O_2]+k''[Cl_2]}\simeq\frac{k}{k'}I_0,$$

an incorrect result; while the Thon mechanism mentioned on p. 549 leads directly to

$$\frac{d[H_2O]}{dt}=k_1I_0[Cl_2],$$

in agreement with Cremer's experimental result.

Cremer's work (*Z. physikal. Chem.*, **128,** 285, 1927) on sensitised water formation is of considerable interest. He finds that the quantum yield of the process (molecules H_2O formed per quantum) is two, and, within the somewhat large experimental error, is independent of the experimental conditions. The latter statement finds expression in the Cremer equation for water formation, viz.

$$\frac{d[2H_2O]}{dt}=k_w[Cl_2],$$

since the rate of absorption of energy is proportional to $[Cl_2]$ and hence the quantum yield is constant. The experimental result of a quantum yield of two is predicted by the Cremer reaction mechanism, since it yields the result that $k_w=k_1I_0$. Thus, taking the principal reactions of the first Cremer mechanism (cf. p. 556)

$$(1)\ Cl_2 + h\nu \rightarrow Cl^* + Cl$$
$$(2)\ Cl^* + Cl_2 \rightarrow Cl_3^*$$
$$(3)\ Cl_3^* + H_2 \rightarrow 2HCl + Cl^*$$
$$(4)\ Cl^* + O_2 \rightarrow O_2^* + Cl$$

together with

$$(7)\ O_2^* + 2H_2 \rightarrow 2H_2O,$$

we obtain

$$\frac{d[2H_2O]}{dt} = k_1I_0[Cl_2].$$

It will be at once apparent how this mechanism predicts a constant quantum yield of two for sensitised water formation. The chain reactions (2) and (3) continue with formation of HCl until the chain is broken by reaction (4) which, necessarily followed by (7), yields two water molecules. Each chain initiated by absorption of a quantum thus forms a large † number of HCl molecules and two water molecules. It is true that the predicted velocity of water formation will be somewhat modified on introducing into the scheme the subsidiary processes (5), (6), and (9), but, as Cremer shows, the effect is a small one. Indeed if, as is believed to be the case under Thon's experimental conditions, k_6 may be entirely neglected, and the O_2 concentration is not exceedingly small so that k_9 becomes of significance, we still obtain (i.e. with reactions (1), (2), (3), (4), (5), and (7)) exactly

$$\frac{d[H_2O]}{dt} = k_1I_0[Cl_2].$$

Theories of the Rôle of Water in the Hydrogen-Chlorine Reaction.—The observations of Coehn and his co-workers Tramm, Jung, and Heymer on the influence of water on the rate of combination of hydrogen and chlorine in visible and in ultra-violet light have evoked much speculation and discussion. The theories relating to the rôle of water in the photo-reaction are numerous, and an extensive literature on the subject has already appeared. In view of the marked interest displayed in the phenomenon and of the conflicting views expressed, there appears every likelihood in the near future of still further contributions to the literature of the subject.

The experimental results on which these theories are based have already been indicated. Briefly they are

(1) That in visible and long wave ultra-violet light, no photo-combination occurs when the partial pressure of water vapour is reduced to 10^{-7} mm.; for values of p_{H_2O} between 10^{-7} and 10^{-4} or 10^{-5} mm. the rate of reaction is a function of the water vapour content; while for partial pressures of water greater than 10^{-4} mm. the reaction velocity is independent of the partial pressure of water.

(2) That the quantum yield in damp mixtures of hydrogen and chlorine is high (Coehn finds $\gamma = 10^4$) both in visible light and in ultra-violet light ($\lambda = 253\ \mu\mu$).

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† Large, at least, when $[O_2]$ is small.

(3) That in short wave ultra-violet light ($\lambda = 253\ \mu\mu$) with *dry* gas mixtures ($p_{H_2O} = 10^{-7}$ mm.) photo-combination occurs, but with a very small quantum yield ($\gamma < 8$).

Recent work of Kornfeld and Steiner (*Z. Physik*, **45,** 325, 1927) demonstrates that the maximum wave-length which initiates reaction in the dry gas is somewhat greater than that stated by Coehn. The latter gives 300 $\mu\mu$ as the limiting wave-length, while Kornfeld and Steiner find that light of wave-length 313 $\mu\mu$ is effective.

The hydrogen-chlorine reaction is not the only photochemical process whose velocity is markedly influenced by traces of water, though it is the most studied and one of the most striking cases. Tramm (*Z. physikal. Chem.*, **105,** 356, 1923) has carefully investigated the effect of removal of moisture on other photochemical gas reactions; he has shown (see p. 629) that water vapour exerts a positive catalytic effect on a number of reactions, a retarding effect in one case (the photo-decomposition of CO_2), while in others an influence of desiccation is absent or at least not yet demonstrated. It cannot be said that for any of the reactions in which a positive (or negative) effect of water has been demonstrated do we know the mechanism of the catalytic action exerted by water vapour. Tramm suggests that in certain cases water acts on foreign molecules in virtue of high dipole moment and strong field, causing enhanced (or decreased) chemical reactivity in those molecules within its sphere of action, while in other processes the assumption of a reaction scheme involving water with formation of intermediate compounds appears plausible.

Reverting to the hydrogen-chlorine reaction, the various theories of the action of water may roughly be classified as follows :—

(*a*) Those theories in which a "physical" action of water on the primary process is postulated. It is assumed in these theories that in the absence of water the "primary" action of light differs from that when water is present. Such views have been advocated by Weigert, Thon, and Lewis and Rideal.

(*b*) Theories in which definite chemical reactions are suggested for the action of water, which action, however, is still located before the chain mechanism (Stern and Volmer, D. L. Chapman).

(*c*) Theories in which H_2O is postulated as an essential reactant in one or more chain processes (Coehn).

(*d*) Theories in which is postulated a "physical" action of water on the velocity of one of the chain reactions (Cathala, Kornfeld).

(*e*) Miscellaneous theories in which a surface action is assumed (Bowen, Norrish).

The theories under (*a*) have to some extent been discussed in a previous section of this Chapter and little further need be added. They postulate an action of water on the primary process, and indeed water may be regarded as part of the absorbing entity. While Weigert assumes the absorbing complex to be H_2—H_2O—Cl_2, Lewis and Rideal postulate a hydrate of chlorine, and Thon regards the action of water as "physical" in the sense indicated by Tramm. As previously stated, all such theories may be discounted if one accepts the interpretation of Kuhn and of Kistiakowsky of their experiments on the absorptions of dry and of damp chlorine. No difference between the two is detectable, and the same result has been confirmed by Kornfeld and Steiner (*Z. Physik*, **45**, 325, 1927), who also adopt the same view that the primary process (dissociation of Cl_2 into Cl* and Cl) is unaffected by drying. Kornfeld and Steiner determined the position of the band convergence limit of chlorine and found that in a hydrogen-chlorine mixture so dry that no reaction occurred on illumination with visible light, the same limit obtained as in moist chlorine.†

The work of Kuhn, Kistiakowsky, and Kornfeld and Steiner also tells against the theories classified under (*b*). In these, the formation of the "active" substance requires the intervention of water, though the latter is not concerned with the light absorption. Chapman's theory is an "activated molecule" theory, and no convergence limit is to be anticipated either with damp or with dry chlorine, while, according to the views of Stern and Volmer (*Z. wiss. Phot.*, **19**, 275, 1920), the formation of chlorine atoms is only possible in the presence of water. The latter suggest a mechanism which is represented by the scheme

$$\begin{array}{ll} (1)\ Cl_2 + h\nu \rightarrow Cl_2^*; & (2)\ Cl_2^* + H_2O \rightarrow HCl + OH + Cl; \\ (3)\ Cl + H_2 \rightarrow HCl + H; & (4)\ H + Cl_2 \rightarrow HCl + Cl; \\ (5)\ OH + H_2 \rightarrow H_2O + H; & (6)\ H + O_2 \rightarrow HO_2. \end{array}$$

Water thus enters into what may be regarded as the primary process, and not into the chains. Since water is regenerated by (5), $[H_2O]$ will not appear in the expression for the reaction velocity, and above a certain limiting concentration the velocity should be independent of $[H_2O]$. Below this limiting concentration, however, the reaction

$$Cl_2^* \rightarrow Cl_2 \text{ or } Cl_2^* + Cl_2 \rightarrow 2Cl_2$$

becomes of importance, and the dependence of the velocity of HCl formation on the concentration of water vapour may be shown to be of the form

$$\frac{k'[H_2O]}{k'' + [H_2O]},$$

which is not in disagreement with the experimental evidence.

Chapman (*Trans. Faraday Soc.*, **21**, 547, 1926) has modified his activated molecule theory of the reaction (cf. p. 548) in order to introduce an explanation of the effect of water vapour. He suggests the scheme

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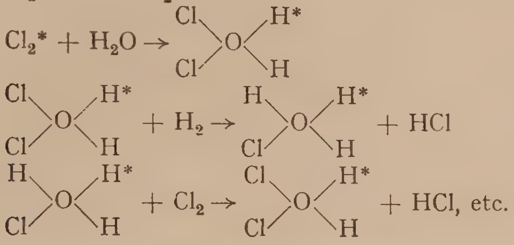
† They also confirmed Coehn and Heymer's observation that in *ultra-violet* light the quantum efficiency of the H_2—Cl_2 reaction is small when the gases are dry. They obtained quantum yields between 1·8 and 9·4 for light of wave-length 265-254 $\mu\mu$, and 6-7 for light of 313 $\mu\mu$.

$$Cl_2 + h\nu \rightarrow Cl_2^*$$



In his original hypothesis, Cl_2^* and HCl^* were postulated in place of the unstable hydrates of Cl_2 and HCl.

(*c*) The theory of Coehn and Jung (*Ber.*, **56,** [*B*], 696, 1923) is of considerable interest and most of the discussion has centred on it. As the theory is a sharply formulated one, it is perhaps more open to attack than other hypotheses of the action of water, and it has consequently been subjected to some criticism. Coehn and Jung put forward two mechanisms: (A) for the photochemical reaction in visible light in presence of water vapour, and (B) for the photo-combination in ultra-violet light in the absence of water.

(A)

$$\begin{array}{l} Cl_2 + h\nu \text{ (small)} \rightarrow Cl_2' \\ Cl_2' + Cl_2 \rightarrow 2Cl + Cl_2 \\ \left.\begin{array}{l} Cl + H_2O \rightarrow HCl + OH \\ OH + H_2 \rightarrow H_2O + H \\ H + Cl_2 \rightarrow HCl + Cl \end{array}\right\} \text{chain reactions} \\ \quad \text{etc.} \end{array}$$

(B)

$$\begin{array}{l} Cl_2 + h\nu \text{ (large)} \rightarrow Cl_2'' \\ Cl_2'' + Cl_2 \rightarrow 2Cl + Cl_2 \\ Cl_2'' + H_2 \rightarrow Cl_2 + 2H \\ H + Cl_2 \rightarrow HCl + Cl \\ Cl + Cl \rightarrow Cl_2 \end{array}$$

It will be noticed that (A) is a chain mechanism while (B) is not. The chain is due to the formation of OH radicals and H atoms by the intervention of water. The presence of water is necessary for the appearance of a chain according to Coehn and Jung, since these investigators exclude the first of the Nernst chain reactions $Cl + H_2 \rightarrow HCl + Cl$. For the same reason, water is required for the occurrence of *any* photo-combination in visible light. In ultra-violet light, however, the larger quantum absorbed by the chlorine makes possible a photo-sensitised decomposition of hydrogen into atoms on collison of Cl_2'' and H_2 (compare the Cario-Franck dissociation of H_2 in the presence of optically excited mercury vapour). The maximum quantum yield predicted on the basis of mechanism (B) is 2, which is—at least in order of magnitude—that found by Coehn and Heymer and by Kornfeld and Steiner.

The theory is an interesting one and of great simplicity. It postulates three wave-length zones for the hydrogen-chlorine reaction :—

(α) No reaction should occur using wave-lengths greater than that corresponding to the heat of dissociation of chlorine.

(β) For wave-lengths between those corresponding to the heats of dissociation of chlorine and of hydrogen, reaction should take place only in the presence of water vapour.

(γ) For wave-lengths less than that corresponding to the heat of dissociation of hydrogen, reaction should occur in the absence of water, but no chain should be formed.

As previously mentioned, the evidence in respect of (α) is not decisive. Coehn and Jung claim to have established a threshold frequency for the reaction not very far different from the anticipated value; Weigert and Nicolai, however, state that reaction is still possible with light of smaller frequencies. With regard to (β) and (γ), if we take the heat of dissociation of hydrogen to be 100,000 cal., we find that the greatest wave-length which should initiate reaction in the *dry* gas mixture is about 284 $\mu\mu$, while Kornfeld and Steiner find that light of wave-length 313 $\mu\mu$ is effective. The theory is thus not in very good accord with experiment from the point of view of wave-length limits.

Coehn's theory of the rôle of water in the reaction mechanism has been criticised by Thon (*Fortschritte der Chemie*, **18,** Heft 11, 1926), Cathala (*Compt. rend.*, **181,** 33, 1925; *J. Chim. phys.*, **23,** 78, 1926; *Bull. Soc. chim.*, **39,** 612, 1926), and Norrish (*Trans. Faraday Soc.*, **21,** 575, 1926). Thon attempts to calculate on the basis of Coehn's theory the dependence of the reaction velocity on the partial pressure of water, and shows that it is difficult to obtain an expression compatible with experiment. He further draws attention to a difficulty involved in the type of "intermediate compound" theory of catalysis which is postulated. The reactions

$$(a)\ Cl + H_2O \rightarrow HCl + OH$$
$$(b)\ OH + H_2 \rightarrow H_2O + H$$

yield, in their sum, the process

$$Cl + H_2 \rightarrow HCl + H,$$

whose direct occurrence is denied. The heat effect associated with the last of these reactions is in the neighbourhood of zero, and thus, while one of the reactions (a) and (b) is exothermic, the other is endothermic. If the endothermicity is considerable, as might well be, it is difficult to see how the reaction could occur sufficiently fast to work a chain.

The main objection to the Coehn theory is, however, that adduced by Cathala, Norrish, and Kornfeld, and lies in the fact that if water enters into reaction in each link in the chain, it is difficult to see how the necessary number of collisions (of water molecules) can occur in gas mixtures containing low partial pressures of water vapour. Cathala calculates that in one experiment of Coehn's in which $p_{H_2O} = 10^{-5}$ mm., the number of quanta absorbed per second $= 6 . 10^{12}$, while the amount of HCl formed per second = $16 . 10^{16}$ molecules. He further estimates that the concentration of H_2O was $3{\cdot}3 . 10^{12}$ molecules per c.c., and that during illumination that of chlorine atoms was $12 . 10^{12}$ atoms per c.c.* The number of collisions between chlorine atoms and water molecules is thus

$$k \times 3{\cdot}3 \times 10^{12} \times 12 \times 10^{12} = k \times 40 \times 10^{24},$$

while that between two chlorine atoms is

$$k' \times (12 \times 10^{12})^2 = k' \times 144 \times 10^{24}.$$

Now, since the quantum yield of the process is 10^4 (chain length $0{\cdot}5 \times 10^4$), the ratio of effective collisions of the first type to effective collisions of the second type must be $0{\cdot}5 . 10^4$. This cannot be the case unless collisions between two chlorine atoms are exceedingly ineffective in forming chlorine molecules. Norrish has extended Cathala's calculations in the following way. He finds (assuming Coehn's mechanism to hold) that if every collision between Cl and H_2O leads to the formation of HCl and OH, then only one collision in 26,000 between chlorine atoms results in recombination. He attempts further to show that this result is incompatible with Bodenstein and Taylor's observations on the rate of decay of the activity of illuminated chlorine, but, in our opinion, unsuccessfully. It has already been shown (p. 541) that in pure chlorine (free from oxygen), *even if every collision between chlorine atoms were accompanied by recombination*, positive results should be obtained in experiments of the type made by Bodenstein and Taylor. The negative result found by Marshall (who used chlorine containing very little oxygen) cannot thus be taken as giving any information regarding the efficiency of collisions between chlorine atoms in producing chlorine molecules, though it *might* be regarded as evidence against the occurrence of chlorine atoms in illuminated chlorine.

Kornfeld (*Z. physikal. Chem.*, **131,** 97, 1927) agrees with Coehn and Jung that water does not affect the primary process and that each link in the chain must be influenced by water ; on the other hand, the possibility of water reacting in the manner postulated by the Coehn-Jung theory is held to be remote for the following reason. Weigert and Kellermann (*Z. physikal. Chem.*, **107,** 1, 1923) have shown that the mean life of a chain in a sensitive mixture of hydrogen and chlorine lies between $\frac{1}{20}$ and $\frac{1}{100}$ sec. Assuming that in the mixture used by Weigert and Kellermann the quantum yield was in the neighbourhood of 10^4, then 10^4 reaction links must occur in a time of at most $\frac{1}{20}$ sec., or each link is completed in $5 . 10^{-6}$ sec. According to Coehn's mechanism, therefore, each chlorine atom must have the opportunity to collide with a water molecule at least $2 . 10^5$ times per second if the reaction is to be independent of p_{H_2O}. According to Coehn and Jung's measurements, the latter condition is fulfilled at $p_{H_2O} = 10^{-5}$ mm. Yet at this pressure of water vapour, a chlorine atom suffers only about 10^2 collisions per second with water molecules, if one calculates with molecular diameters as given by the kinetic theory of gases. The discrepancy is striking, and, unless there is some unsuspected error in these calculations, the result must be regarded as strong evidence against the validity of the Coehn-Jung theory.

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* How this value was obtained is not indicated. As shown by Norrish, however, a figure substantially the same is found by equating the number of collisions between Cl and H_2O to half the number of HCl molecules formed, assuming reasonable values for the diameters of Cl atoms and H_2O molecules.

(*d*) Cathala supposes that water exerts an influence on one of the reactants (of a chain process) in its vicinity. In virtue of its being an electric dipole with a large stray field, a water molecule is supposed to be capable of influencing the structure of other molecules within a given sphere of action and enhancing their reactivity. He further presumes that it is the chain reaction (of the Göhring mechanism)

$$Cl_3 + H_2 \rightarrow 2HCl + Cl$$

which is so influenced, and that it is the hydrogen molecule which is affected. We need not, however, reproduce this author's calculations, as they appear to us to be unsound. For example, he considers that the velocity of photo-combination of hydrogen and chlorine is proportional to the $\frac{3}{2}$ power of the light intensity, a result which he deduces by an incorrect derivation from the Göhring mechanism together with the assumption that the catalytic activity (and the sphere of influence) of water molecules is proportional to the light intensity. If we disregard this assumption, however, Cathala's theory is essentially identical with that recently advocated by Kornfeld. The latter also postulates an action by water on a chain reaction, such, for example, as the chain reaction of the Cremer mechanism

$$Cl_3^* + H_2 \rightarrow 2HCl + Cl.$$

The additional assumption is necessary, however, that the water molecule exerts an influence on molecules many molecular diameters distant from it. From Kornfeld's calculations (see preceding paragraph) it follows—if this hypothesis be accepted—that the water molecule is active at a distance which is at least $\sqrt{10^3}$, i.e. 30 times the ordinarily accepted value of its radius and probably at considerably greater distances. Kornfeld does not specify more closely the nature of the action exerted by the water molecule; all that is postulated is that in this and other reactions in which traces of water profoundly modify the velocity the sphere of action of the water molecule is much greater than its ordinary *sphère de choc*. In this connection it is not without interest that in other cases of energy transfer in gaseous systems, much greater values have been calculated for "collisional" diameters than those derived from the kinetic theory of gases. Brief mention of such cases has been made in Chapter V.†

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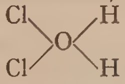
† Cf. also Nordheim, *Z. Physik*, **36**, 496, 1926; Schütz, *ibid.*, **35**, 260, 1925; and Datta, *ibid.*, **37**, 625, 1926.

(*e*) Other theories of the rôle of water in the hydrogen-chlorine reaction are those of Norrish (*Trans. Faraday Soc.*, **21,** 575, 1926) and of Bowen (*J.C.S.*, **125,** 1233, 1924), both of whom postulate a surface action. Norrish rejects Cathala's theory, owing to the very large sphere of action which must be ascribed to the water molecule. He discusses the experimental arrangement of Coehn and Jung for determining the influence of water on the reaction, and considers that under the conditions of this investigation the reaction vessel would be just covered with a monomolecular film of water vapour at some (apparent) pressure of water vapour between 10^{-5} and 10^{-7} mm., while in the experiments with greater partial pressures of water, water vapour will also be present in the gas phase. He assumes that the primary process takes place only in the adsorbed water film, and consists in the expulsion of Cl atoms from a complex  assumed to be present in the film. The Cl atoms so formed enter the gas phase and Nernst chains ensue, which extend into the gas mixture until they are brought to an end by meeting a vessel wall. As already mentioned, however, this interesting theory has been disproved by the work of Coehn and Heymer, who showed that photo-combination of hydrogen and chlorine takes place in visible light in the absence of any solid or liquid surface.

Bowen suggested that water acted in manner similar to that suggested by Wood (*Proc. Roy. Soc.*, **102** A, 1, 1922) for its influence on the yield of hydrogen atoms obtained in the Geissler tube discharge. On a clean dry surface hydrogen atoms readily combine, but not on a surface covered with an adsorbed water film. According to Bowen, the chains in the H_2—Cl_2 reaction are thus rapidly ended in absence of water, with consequent poor quantum yield. Chapman (*loc. cit.*) shows, however, that this theory is untenable, since it entails a mean life for a chain much longer than is consistent with experiment.

The above are the chief suggestions so far advanced to explain the catalytic action of water in the hydrogen-chlorine reaction. Summing up, we may say that objections have been urged against all theories, several of which may be regarded as definitely ruled out. Possibly the most satisfactory hypothesis at present is that of Kornfeld and Cathala, involving an ill-defined " action at a distance " by water molecules on a chain reaction. Clearly, however, further work is necessary before any theory can be considered as other than a working hypothesis.

With regard to the part played by water in the reaction in ultra-violet light, we might suggest the following in lieu of the Coehn-Jung mechanism. The latter postulates as primary process (in both visible and ultra-violet light) the formation of an activated chlorine molecule, which then dissociates a chlorine molecule into atoms on collision, or (when ultra-violet light is used) dissociates a hydrogen molecule. Recent work, however, makes it probable (at least for visible and long wave ultra-violet light) that optical dissociation of Cl_2 molecules takes place in a single act without collision. In order to account for the reaction in ultra-violet light in absence of water, we might assume either

(*a*) that optical dissociation in one elementary act occurs and that the Cl atoms so formed part with such a velocity that they are enabled to react with hydrogen according to

$$Cl + H_2 \rightarrow HCl + H,$$

a reaction which (we might assume with Coehn) does not otherwise occur; or

(*b*) that, as in the case of I_2 with ultra-violet light, dissociation does not occur in one elementary act, but that the activated chlorine molecules primarily formed either dissociate hydrogen on collision or yield atoms with high kinetic energy on colliding with chlorine.

The net result of either hypothesis will be similar to that of Coehn's, but each avoids the objection urged by Lewis (*Nature*, **120,** 473, 1927) against the latter theory, viz. that in the dry gases using ultra-violet light a quantum yield less than unity might be anticipated on Coehn's mechanism if the ratio hydrogen/chlorine be small.

THE PHOTOCHEMICAL FORMATION OF PHOSGENE.

The photochemical union of CO and Cl_2 is another complicated process which resembles in many ways the hydrogen-chlorine reaction. Both reactions are associated with high quantum yields, both are retarded by oxygen and positively catalysed by water vapour, and induction periods—presumably due to the same underlying causes—may occur in either when impure gas mixtures are employed. The hydrogen-chlorine reaction appears, however, to be the more extreme case; it has a greater quantum yield than the $CO—Cl_2$ reaction, its induction periods are more marked, retardation by oxygen is more strongly developed, and the effect of extreme desiccation is more drastic. It is not improbable that both reactions have mechanisms of an essentially similar type, but as yet both processes—especially the photo-union of CO and Cl_2—are incompletely studied, and it would be premature at present to do more than indicate the general resemblances between the two.

The photochemical combination of carbon monoxide and chlorine was discovered by Davy in 1812, but it was little studied until the present century, when investigations were initiated by Dyson and Harden (*J.C.S.*, **83,** 201, 1903), Wildermann (*Trans. Roy. Soc.*, **199**A, 337, 1902; *Z. physikal. Chem.*, **42,** 257, 1903), and Chapman and Gee (*J.C.S.*, **99,** 1726, 1911). Dyson and Harden's work was concerned with the induction period, which, in the light of the later work of Burgess and Chapman, must be attributed to impurities. Wildermann investigated the kinetics of the reaction and found that with constant light intensity and feeble absorption by the chlorine the reaction rate is given by

$$\frac{dx}{dt} = k[Cl_2][CO],$$

i.e. by the mass-action expression. But few experiments were carried out, however, and later work has demonstrated that the reaction course is certainly more complex. Chapman and Gee studied the effects of certain additions — in especial that of oxygen — on the initial velocity of reaction. They found that the sensitivity (S) (initial rate of reaction) may be expressed by an equation of the type $S = A + \frac{B}{[O_2]}$, in which A and B are constants. The retarding effect of oxygen is thus less persistent than in the hydrogen-chlorine reaction; it is now relatively greater when oxygen is present in small amounts. These observations form insufficient basis for suggesting possible reaction mechanisms; the recent work of Bonhoeffer (*Z. Physik*, **13,** 94, 1923) and of Bodenstein and his pupils (*Rec. trav. chim.*, **41,** 565, 1922; *Sitzungsber. Preuss. Akad. Berlin*, p. 104, 1926; *Z. physikal. Chem.*, **129,** 241, 1927; *ibid.*, **130,** 422, 1927; *ibid.*, **131,** 153, 1928) has, however, shed more light on the subject, and it is believed that, in spite of difficulties experienced in obtaining reproducible results, sufficient reliable data have been gathered to enable us to speculate with regard to the processes operating in the reaction, at least when it is carried out at ordinary temperatures.

Dealing first with the investigations of Bodenstein and his co-workers, and considering now their experiments at room temperature with mixtures containing but little oxygen, the following results were obtained.

(1) In mixtures of equivalent quantities of chlorine and carbon monoxide and with light of constant intensity between the wave-lengths 405 $\mu\mu$ and 460 $\mu\mu$, the rate of combination is given by

$$\frac{dx}{dt} = k'[Cl_2]^2.$$

The "constants" calculated in this way are, however, not constant in any given experiment. They increase somewhat from the start, pass through a maximum, and then slowly decrease. The initial increase in k' is attributable to removal of the retarding oxygen by a simultaneous sensitised reaction forming CO_2. This was confirmed by the results of experiments in which known small amounts of oxygen were added to mixtures of CO and Cl_2; it was then found that the greater the oxygen content, the lower was the initial value of k' and the longer was the time taken to reach the (same) maximum value. The cause of the fall in k' towards the end of an experiment will be discussed later.

(2) Experiments with non-equivalent amounts of CO and Cl_2 showed that the kinetic equation is

$$\frac{d[COCl_2]}{dt} = k'[Cl_2]^{\frac{3}{2}}[CO]^{\frac{1}{2}}.$$

(3) In all experiments the absorption of light by the chlorine was weak, and the energy absorbed was thus proportional to $I_0[Cl_2]$. Experiments using light of different intensities led to the expression

$$\frac{d[COCl_2]}{dt} = kI_0^{\frac{1}{2}}[Cl_2]^{\frac{3}{2}}[CO]^{\frac{1}{2}} = k\sqrt{E_{abs.}}[Cl_2][CO]^{\frac{1}{2}},$$

in which $E_{abs.}$ is the energy absorbed.

(4) The quantum yield of the process is high. Bonhoeffer (*loc. cit.*) found $\gamma = 2{\cdot}6 \,.\, 10^3$, Kahle (cf. Bodenstein, *Rec. trav. chim.*, **41**, 565, 1922) found $\gamma = 1{\cdot}5 \,.\, 10^3$, and Bodenstein, employing a gas mixture in which the partial pressures of Cl_2 and CO were each $\frac{1}{2}$ atm., but which was presumably freer from oxygen than those previously used, found $\gamma = 7{\cdot}3 \,.\, 10^3$.

These observations relate to experiments at room temperature and to mixtures not excessively dry (dried over concentrated sulphuric acid); we will discuss later the behaviour of CO—Cl_2 mixtures at high temperatures and also the photosensitised reaction taking place in the presence of oxygen. In interpreting the above results, Bodenstein and Heisenberg postulate a reaction scheme which (*a*) assumes as primary process the formation of activated chlorine molecules, and (*b*) assumes that the reaction proceeds *via* Cl_3 molecules, a theory already applied with success to the kinetics of the thermal formation of phosgene at temperatures between 300° and 500° C. The theory now proposed necessarily differs, however, from that suggested for the thermal reaction, since in the latter the velocity is found to be proportional to [CO] while the photochemical rate is proportional to $[CO]^{\frac{1}{2}}$. The complete scheme now suggested is

(1) $Cl_2 + h\nu \rightarrow Cl_2^*$
(2) $Cl_2^* + CO \rightarrow CO^* + Cl_2$
(3) $Cl_2^* \rightarrow 2Cl$
(4) $Cl + Cl_2 \rightarrow Cl_3$
(5) $Cl_3 + CO \rightarrow COCl_2 + Cl$
(6) $Cl_3 \rightarrow Cl_2 + Cl$
(7) $Cl + Cl \rightarrow Cl_2$.

This is a chain process, since (5) regenerates chlorine atoms which may again react to form Cl_3, etc. Process (2) is a retardation; it may be written as above, or one might even assume that $COCl_2$ results from it, but in the latter event the reaction is still a retardation since only one molecule of $COCl_2$ is formed instead of the thousand or so which could result had reaction proceeded *via* the chain including process (5).

The mechanism yields

$$+\frac{d[COCl_2]}{dt} = \frac{k_4k_5[Cl_2][CO]}{k_5[CO] + k_6} \cdot \sqrt{\frac{k_1k_3I_0[Cl_2]}{k_7(k_2[CO] + k_3)}}.$$

If now we may neglect k_5 [CO] compared with k_6 and also k_3 compared with k_2[CO], we obtain

$$+\frac{d[\mathrm{COCl_2}]}{dt}=\frac{k_4k_5\sqrt{k_1k_3}}{k_6\sqrt{k_7k_2}}\cdot\sqrt{k_1I_0[\mathrm{Cl_2}]}\cdot[\mathrm{Cl_2}]\cdot[\mathrm{CO}]^{\frac{1}{2}},$$

in agreement with experiment.

Bodenstein justifies the above assumptions by correlating in the following way the observed rate of photochemical combination with observations on the velocity of the thermal reaction. The mechanism suggested for the latter, and which accounts very well for all the experimental observations, is (1′) $Cl_2 \rightarrow 2Cl$, together with reactions (4), (5), (6), and (7) of the photochemical reaction scheme above. Processes (1′) and (7) and (4) and (6) are opposing reactions which constantly maintain the corresponding equilibria, and the total velocity (of the thermal process) is determined by reaction (5). It may be demonstrated with some plausibility (Bodenstein and Plaut, *Z. physikal. Chem.*, **110,** 399, 1924) that in (5) every collision is effective, a conclusion to be anticipated for an exothermic double decomposition involving the atom-like, unstable molecule Cl_3. Returning now to the expression derived for the photochemical reaction rate, this may be written in the form

$$+\frac{d[\mathrm{COCl_2}]}{dt}=k_5\cdot\frac{k_4}{k_6}\cdot[\mathrm{CO}]\cdot[\mathrm{Cl_2}]\cdot\sqrt{\frac{k_3}{k_2[\mathrm{CO}]}}\cdot\sqrt{k_1I_0[\mathrm{Cl_2}]}\cdot\sqrt{\frac{1}{k_7}}.$$

In this equation k_5 is a collision number, and k_4/k_6 is an equilibrium constant which may be roughly estimated from Bodenstein and Plaut's calculations of the equilibrium $3Cl_2 \rightleftharpoons 2Cl_3$ and the equilibrium constant of the reaction $Cl_2 \rightleftharpoons 2Cl$ (Wohl and Kadow, *Z. physikal. Chem.*, **118,** 460, 1925). The factor k_3/k_2[CO] must, conforming to the assumption made above, be small, yet certain results mentioned later indicate that it is not exceedingly small. Bodenstein makes it equal to 10^{-2} when $p_{\mathrm{CO}} = 380$ mm.; since it only enters as a square root term, an uncertainty in this estimate is without serious effect. $k_1I_0[\mathrm{Cl_2}]$ is the number of quanta absorbed per second, and finally k_7 is the rate of recombination of chlorine atoms. If in this every collision results in combination, k_7 is then simply a collision number. But as we have seen (cf. Chapter VIII.), in the analogous reaction between bromine atoms only one collision in 800 is effective, in spite of the fact that the total gas concentration might be anticipated to be sufficiently great to enable the freshly formed halogen molecules to lose or to quantise their excess energy as a result of collision. We should therefore in the case of chlorine try both assumptions, either all collisions between Cl atoms effective, or only a fraction of $\frac{1}{800}$. For a certain experiment in which the partial pressures of CO and Cl_2 were each $\frac{1}{2}$ atm. and the temperature 300° Abs., we find, after inserting the values $k_5 = 2{\cdot}6\,.\,10^{31}$, $k_4/k_6 = 7{\cdot}5\,.\,10^{-5}$, $[\mathrm{CO}] = [\mathrm{Cl_2}] = 0{\cdot}5$,

$\sqrt{\frac{k_3}{k_2[\mathrm{CO}]}} = 10^{-1}$, and $\sqrt{\frac{1}{k_7}} = (0{\cdot}28$ *or* $7{\cdot}8)\,.\,10^{-15}$, that number of molecules of CO formed

$$= (1{\cdot}4 \textit{ or } 38) \,.\, 10^{10} \times \sqrt{\text{number of absorbed quanta.}}$$

In this experiment the number of quanta absorbed was $2{\cdot}2 \,.\, 10^{15}$ and the yield of $COCl_2$ was $1{\cdot}6 \,.\, 10^{19}$ (corresponding to $\gamma = 7{\cdot}3 \,.\, 10^3$), while the calculated yield is $6{\cdot}4 \,.\, 10^{17}$ or $1{\cdot}8 \,.\, 10^{19}$. The latter figure agrees well with the experimental value and it would appear, in spite of the admitted uncertainties in the calculations together with the fact that it is somewhat difficult to disentangle the various assumptions made, that the mechanisms proposed for the thermal and photochemical reactions do form a consistent whole. It has been assumed in the above that $k_5[CO]$ is much less than k_6. That this assumption is justified is shown by Bodenstein in the following way. k_5 is a collision number which, at a temperature of 300° Abs., has the value $2{\cdot}6 \,.\, 10^{31}$. Hence, with $[CO] = \frac{1}{2}$ atm., $k_5[CO] = (2{\cdot}6 \,.\, 10^{31}) \times (\frac{1}{2}$ atm.). k_6 may be calculated from the equation

$$k_6 = \frac{k_4[Cl] \,.\, [Cl_2]}{[Cl_3]},$$

i.e. postulating that the equilibrium $Cl_2 + Cl \rightleftharpoons Cl_3$ is continually maintained. Now k_4 is certainly a collision number, and, introducing for [Cl] and $[Cl_3]$ the values calculated for 300° Abs. on the basis of the equilibria $Cl_2 \rightleftharpoons 2Cl$ and $3Cl_2 \rightleftharpoons 2Cl_3$ already employed, we obtain

$$k_6 = \frac{2{\cdot}6 \,.\, 10^{31} \times 4 \,.\, 10^{-19} \times (\frac{1}{2} \text{ atm.})}{1{\cdot}5 \,.\, 10^{-23}} = 2{\cdot}6 \,.\, 10^{31} \times 3 \,.\, 10^4 \times (\tfrac{1}{2} \text{ atm.}),$$

i.e. a value $3{\cdot}4 \,.\, 10^4$ times as great as $k_5[CO]$. The mechanism may also be tested in another way by calculating the temperature coefficient it predicts for the reaction and comparing it with that found experimentally. We may write

$$\frac{d[COCl_2]}{dt} = \frac{k_4}{k_6} \,.\, \sqrt{k_3} \,.\, \left([CO]^{\frac{1}{2}}[Cl_2] \,.\, \sqrt{k_1 I_0 [Cl_2]} \,.\, \frac{k_5}{\sqrt{k_2} \,.\, \sqrt{k_7}}\right).$$

The quantities inside the round brackets are all independent of temperature *; the temperature coefficient of the total reaction will thus be determined by the variation of $k_4/k_6 \,.\, \sqrt{k_3}$ with temperature. Now k_3 is the constant of the reaction $Cl_2{}^* \rightarrow 2Cl$, and we have no definite knowledge as to how temperature would affect the velocity of such a process. The most probable assumption is that the rate is independent of temperature and that in this particular case every chlorine molecule which is not deactivated by CO or by O_2 decomposes into atoms. Making this assumption, we have then only to consider the variation of k_4/k_6 with temperature. k_4/k_6 is the equilibrium constant of the process $Cl_2 + Cl \rightleftharpoons Cl_3$, and from the results of measurements of the rate of thermal formation of phosgene it may be concluded that the formation of Cl_3 is a slightly exothermic reaction. It follows, therefore, that k_4/k_6 should decrease with increasing temperature, and hence that the photochemical union of CO and Cl_2 should possess a temperature coefficient slightly less than unity. Experiment confirms this, the velocity constant of the reaction falling from 5·3 at $T = 283°$ to 4·4 at $T = 313°$. Also, the magnitude of the decrease appears to be of the predicted order.

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* Assuming that the absorption of light by chlorine is constant.

It has been stated that the constants calculated from the equation $\frac{dx}{dt} = k'[Cl_2]^{\frac{3}{2}}[CO]^{\frac{1}{2}}$ increase somewhat at the start of a given experiment, and that this increase is attributable to a retardation by oxygen which is slowly consumed by a sensitised reaction with formation of CO_2. As a consequence of the slowly diminishing oxygen concentration, the rate of phosgene formation tends to rise. The observation of Chapman and Gee that the retardation is relatively greater at small oxygen concentrations has been confirmed by Bodenstein and his co-workers. This might possibly be due to the relatively greater extent of CO_2 formation at higher concentrations of oxygen, so that the oxygen concentration is more rapidly reduced, causing retardation to be less than would be anticipated on the basis of inverse proportionality between rate of combination of CO and Cl_2 and initial concentration of oxygen. Yet the nature and mechanism of the retardation itself have not been elucidated; the most obvious suggestion that it is essentially due to a reaction

$$(2a)\ Cl_2^* + O_2 \rightarrow Cl_2 + O_2^*$$

does not appear to be in very good agreement with experiment, though, owing to the fact that oxygen retardation is bound up with its consumption, we have not enough data to hand to arrive at a decision on this point.

The fall in the value of the constants towards the end of an experiment may, according to Bodenstein, be explained in terms of the above reaction scheme. It is ascribed to the fact that neglect of the constant k_3 compared with $k_2[CO]$ is only allowable when the concentration of CO is not too small. When, therefore, towards the end of an experiment the concentration of CO is considerably reduced, the constants calculated on the basis that the velocity is proportional to $[CO]/\sqrt{[CO]}$ should tend to fall. This is one reason for the decrease in the constants; another is that it has not been possible to free the reaction vessel completely from inhibiting impurities, and diffusion of the latter from taps, etc. into the main reaction mixture makes itself more and more evident in the later stages of an experiment. For this reason it has not been possible to calculate the ratio of k_3 to $k_2[CO]$ from the rate of diminution of the constants in individual experiments, and thus the value 1/100 for this ratio employed above is a somewhat uncertain estimate.

Though Bodenstein's mechanism, taken as a whole, appears to account satisfactorily for the observed behaviour of CO—Cl_2 mixtures on illumination at room temperatures, it is of course open to the objection that the postulated primary process—an activation of chlorine molecules—is not that to which modern physical work points. The reason for now assuming activation of Cl_2 molecules instead of primary dissociation into atoms "in one elementary act" is the fact that the velocity of the photo-reaction is found to be proportional to $\sqrt{[CO]}$ and not to [CO]. The kinetic expression experimentally obtained may be deduced, still retaining the hypothesis of primary dissociation, in the following way. If, with primary dissociation of chlorine molecules into atoms, one retains processes (4), (5), (6), and (7), but assumes that in the ternary collision necessary for

$$(7)\quad Cl + Cl \rightarrow Cl_2$$

to take place carbon monoxide molecules (and also O_2 molecules) are much more effective than molecules of Cl_2 or of $COCl_2$, one arrives at the right result. Yet, as Bodenstein points out, while one might expect specific effects of different gases in this connection, it is so extremely improbable that the effect of CO should be so overwhelmingly great that this theory is hardly tenable. For this reason he retained the original reaction scheme as the more acceptable.†

Turning now to a brief discussion of oxygen retardation and of the chlorine-sensitised formation of CO_2 in mixtures of CO, Cl_2, and O_2, it is to be observed that oxygen retards phosgene formation only in the photochemical reaction at low and moderate temperatures; neither the thermal reaction (tested between 160° and 450° C.) nor the photo-combination at temperatures higher than 260° C. is affected. Schumacher (*Z. physikal. Chem.*, **129,** 241, 1927), studying the behaviour of $CO—Cl_2—O_2$ mixtures on illumination at room temperature with violet light ($\lambda = 400\text{-}450\ \mu\mu$), obtained the following results:—

(1) Small quantities of O_2(1 mm.) exert a marked retarding effect on the rate of phosgene formation; with increasing p_{O_2} the retardation increases, but slower than proportionally to the oxygen content. The oxygen is simultaneously consumed with formation of CO_2.

(2) In presence of large quantities of O_2 ($p_{O_2} > 100$ mm.) and small concentrations of Cl_2($p_{Cl_2} < 50$ mm.) the sensitised formation of CO_2 is practically the only reaction taking place, the velocity of formation of $COCl_2$ being practically zero. Even in the presence of much greater

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† In this connection Bodenstein suggested that CO(or O_2) molecules might influence the normal primary action of light on Cl_2 molecules (causing retardation of dissociation of Cl_2^* into atoms), and that the effect could be exerted through greater distances than "gas-kinetic" diameters. These gases should thus affect the absorption spectrum of chlorine; but in view of the recent finding of Kornfeld and Steiner and of others that water does not influence the chlorine absorption spectrum, an influence by CO or by O_2 is not very probable. As yet, it cannot be regarded as clear how the observation that the rate of photo-combination of CO and Cl_2 is proportional to $\sqrt{[CO]}$ (and not to [CO]) is to be reconciled with the view that violet light causes primary dissociation of chlorine into atoms.

concentrations of Cl_2, when $p_{O_2} > 100$ mm. the extent of phosgene formation is small.

(3) The sensitised reaction is often associated with an induction due to impurities in the chlorine; this may be obviated by a short pre-illumination of the mixture of CO and Cl_2 (with formation of some phosgene) before adding the oxygen. Reproducible results for the velocity of the sensitised reaction may then be obtained.

(4) The velocity of CO_2 formation is practically independent of p_{O_2} when this is greater than 100 mm. and is also independent of $[COCl_2]$ and of $[CO_2]$. For smaller oxygen concentrations (between 10 mm. and 100 mm.), the velocity is the smaller the less the concentration of oxygen, though the fall in reaction rate is less than that which proportionality between dx/dt and p_{O_2} would demand.

(5) The velocity of sensitised formation of CO_2 in mixtures containing sufficiently high oxygen concentrations ($p_{O_2} > 100$ mm.) is given by

$$+\frac{d[CO_2]}{dt} = kI_0^{0\cdot71}[Cl_2]^{0\cdot71}[CO]^{\frac{1}{2}} = k' \,.\, E_{\text{abs.}}^{0\cdot71} \cdot [CO]^{\frac{1}{2}}.$$

(6) The temperature coefficient of the sensitised reaction is 0·95.

(7) The quantum efficiency of the sensitised reaction is high, and under appropriate conditions is comparable with that of phosgene formation. Thus at room temperature, for a mixture containing sufficient oxygen and in which $p_{CO} = p_{Cl_2} = 380$ mm., the yield of CO_2 is about 1000 molecules per quantum absorbed by the chlorine. The quantum yield of $COCl_2$ in a similar mixture but with no oxygen present is about 3000 ($\lambda = 405\ \mu\mu$ in each case).

It has not been found possible to interpret these observations by a satisfactory theory of the reaction mechanism. The contrast in quantum yields of this sensitised reaction and that occurring in H_2—Cl_2—O_2 mixtures is certainly striking, the former process necessarily demanding interpretation in terms of some chain mechanism. Two such mechanisms may be tentatively suggested, though neither is stated to be satisfactory. They are—

(1) Assuming oxygen retardation to be due to $Cl_2^* + O_2 \rightarrow Cl_2 + O_2^*$, then a chain of some type might follow the reaction $2CO + O_2^* \rightarrow 2CO_2^*$.

(2) Alternatively, however, the direct reaction (formation of phosgene) might occur *via* the intermediate substance COCl (instead of Cl_3), an assumption which appears equally suited to account for the kinetics of both the thermal and the photochemical reaction (cf. Christiansen, *Z. physikal. Chem.*, **103,** 99, 1923; Bodenstein, *Z. physikal. Chem.*, **130,** 422, 1927). A chain leading to CO_2 formation in the presence of oxygen might then be

$$(a)\ COCl + O_2 \rightarrow CO_2 + ClO;\ (b)\ ClO + CO \rightarrow CO_2 + Cl;$$
$$(c)\ Cl + CO \rightarrow COCl.$$

Finally, there remains for discussion the results of experiments on the photo-combination of CO and Cl_2 at high temperatures (Bodenstein and Onoda, *Z. physikal. Chem.*, **131,** 153, 1928). At temperatures between 200° and 300° C., the kinetics of the reaction is quite different from that at room temperature. The kinetic expression which is now obeyed is

$$\frac{dx}{dt} = kI_0[Cl_2]^2[CO] = kE_{abs}\,.\,[Cl_2][CO],$$

and the reaction is no longer retarded by oxygen nor is there any appreciable formation of CO_2 in presence of this gas. This reaction also has a temperature coefficient less than unity and it is accelerated by water vapour. Between 270° and 300° C. the water vapour initially present is slowly removed by the reaction $COCl_2 + H_2O \rightarrow CO_2 + 2HCl$; after removal of the last traces of water vapour, reproducible results for the rate of photo-combination of CO and Cl_2 are obtained. Below 270° the rate of hydrolysis of $COCl_2$ is too small to affect the velocity constants of formation of $COCl_2$; above 300° the hydrolysis is rapidly effected in the first few minutes, and the constants obtained correspond throughout to those of " dry " mixtures.

At still higher temperatures (400° C.) the velocities of the " dark " reactions, formation and decomposition of $COCl_2$, are appreciable, and the observed rate of reaction on illumination is the resultant of the two opposing " dark " reactions, the direct photo-reaction, and the photosensitised reverse decomposition of $COCl_2$.† In agreement with the observations of Weigert (*Ann. Physik*, **24,** 55, 1907), it was found that the photostationary state on illumination is practically identical with the thermal equilibrium state. This is interpreted to mean that the action of light is again different from that in the temperature range 200° to 300°, and now consists essentially in increasing the concentration of Cl atoms, so that the rates of both formation and decomposition of phosgene are increased in the same ratio and consequently no change in the equilibrium conditions ensues. The velocity of phosgene formation both in the dark and in the light is now given by an equation of the type

$$\frac{dx}{dt} = [Cl_2]^{\frac{1}{2}}\{k_b[CO][Cl_2] - k_z[COCl_2]\},$$

and similarly the rate of decomposition of phosgene by the same equation with the sign reversed.

There thus appear to be three different modes of photochemical reaction between CO and Cl_2:—

(*a*) at room temperature and up to 200°, a reaction whose rate is proportional to $[Cl_2]^{\frac{3}{2}}[CO]^{\frac{1}{2}}$ and which is retarded by O_2 with formation of CO_2 by a sensitised reaction;

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† This photosensitised reaction cannot take place at low temperatures.

(*b*) at moderate temperatures between 200° and 300°, a reaction not retarded by oxygen whose velocity is proportional to $[Cl_2]^2[CO]$; and

(*c*) at still higher temperatures (400°), a reaction which is accompanied by the photosensitised reverse process, and whose velocity is proportional to $[Cl_2]$ $[CO]$.

The mechanism of (*c*) appears to be that of the dark reaction (see p. 575), and that of (*a*) has been above discussed. The mechanism of (*b*) is uncertain, except for the fact that it is a chain reaction with a quantum yield in the neighbourhood of 1000.

The influence of water vapour on reaction (*a*)—the reaction at room temperature—is of some interest. Coehn and Tramm (*Z. physikal. Chem.*, **105,** 356, 1923) showed that, unlike the hydrogen-chlorine reaction, reduction of the water content to 10^{-6} mm. does not completely prevent photo-combination of CO and Cl_2 in visible light, though the rate is markedly reduced. Further, Bodenstein indicates that desiccation influences the kinetics of the process, the kinetic equation being altered into that characteristic of reaction (*b*). This result, if substantiated, might be of assistance in elucidating the nature of the rôle played by water in this and other photo-reactions, but it is not yet possible to discuss its significance.

The photochemical formation of phosgene from CO and Cl_2 at room temperature has also been studied by Cathala (*J. Chim. phys.*, **24,** 663, 1927), who used a dynamic method and the full light of a quartz mercury arc as light source. The reaction mixture was prepared by decomposing phosgene at 850°, and, after passing the gas through the illuminated quartz vessel, the ratio of Cl_2 to $COCl_2$ in the issuing gas was determined analytically. Expressing the velocity of reaction in the form

$$\frac{d[COCl_2]}{dt} = k[Cl_2]^m[CO]^n,$$

Cathala believes his results are best satisfied with $m + n = \frac{5}{2}$, m being presumably $\frac{3}{2}$ and n unity as in the kinetic expression for the "dark" reaction. Examination of his data shows, however, that the value $m + n=2$ satisfies his results almost as well; since also in all his experiments equivalent quantities of CO and Cl_2 were necessarily present, his work cannot be regarded as impugning that of Bodenstein with its wider variation of experimental conditions.

CHAPTER XI.

PHOTOSENSITISATION.

A PHOTOSENSITISER may be defined as a substance which, when present in an insolated system, absorbs the activating light without itself suffering permanent change, but permits the absorbed energy to be utilised in initiating chemical reaction between other molecular entities present. Two cases may perhaps be differentiated: (*a*) in the absence of the photosensitiser, no chemical reaction occurs when light is used within the frequency range which is effective when the photosensitiser is added to the system; (*b*) with light of a given frequency, reaction may take place partly as a sensitised, partly as a direct photochemical process. In previous Chapters we have discussed certain examples of photosensitisation; we shall now consider the subject from a general standpoint and deal with further cases. The subject is of dual importance, theoretically because the study of photosensitised processes in relatively simple gaseous systems seems destined to shed much light on the mechanism of photochemical change, and practically owing to technical applications in photography.

The chief characteristic of a photosensitised reaction is that the absorbing substance is not a " stoichiometric " reactant in the process connecting initial and final states, though naturally there are cases known in which the photosensitiser is itself consumed by a " side " reaction. From one point of view photosensitisation often effects a simplification of the conditions of experiment, since in many cases the rate of absorption of radiant energy is constant throughout the experiment, and thus at least one factor tending towards simple reaction kinetics is assured. If this is to be the case, it is of course necessary that the region of light absorption by the photosensitiser lies outside those of the reactants and resultants, and that variation in the concentrations of the latter substances does not affect the absorption of the photosensitiser, which conditions are not always found to hold. In the latter event and when (α) the photosensitiser is consumed by a side reaction or (β) a photosensitiser is formed during the reaction (autosensitisation), complex reaction kinetics may be anticipated.

Examples of photosensitisation are numerous; they include (*a*) gas reactions sensitised by mercury vapour, chlorine, and bromine, (*b*) reactions in liquid media in which the absorbing substances are the halogens, iron salts, uranyl salts, etc., and (*c*) reactions in which solid phases are present, such as sensitisation by zinc oxide, sensitisation of the photographic plate, and the photosynthesis of carbohydrates from CO_2 and H_2O in presence of chlorophyll. Sensitisation was probably first noted by Vogel (*Ber.*, **6,** 1305, 1873) who showed that the photographic plate, which is ordinarily sensitive only to wave-lengths less than 530 $\mu\mu$, may, by addition of certain coloured substances (dyes) to the emulsion, be made sensitive to radiation of greater wave-length which is absorbed by the dye. Other early examples, which are primarily of practical interest, are the oxidation of leuco-bases (Gros, *Z. physikal. Chem.*, **37,** 157, 1901) and the sensitising action of fluorescent bodies on enzymic, bacterial, and other biological processes (Tappeiner and Jodlbauer, *Die sensibilisierende Wirkung fluoreszierender Substanzen*, Leipzig, 1908). The discovery of photosensitisation in homogeneous gaseous systems made by Weigert (*Ann. Physik*, [iv.], **24,** 55, 243, 1907) is of theoretical significance, since the study of simpler sensitised processes such as these is more likely to afford an insight into the reaction mechanism. Weigert found that the following reactions are sensitised by the addition of chlorine:—

$$(1)\ COCl_2 \rightarrow CO + Cl_2,\ (2)\ 2O_3 \rightarrow 3O_2,\ (3)\ 2H_2 + O_2 \rightarrow 2H_2O,$$
$$(4)\ 2SO_2 + O_2 \rightarrow 2SO_3,$$

i.e. all these reactions take place in presence of chlorine when illuminated by blue or violet light which is absorbed by the sensitiser (Cl_2). Of these reactions, the sensitised decomposition of ozone is of peculiar interest, as also is the same reaction sensitised by bromine. The difference in the quantum sensitivities of the two processes forms an unsolved problem of importance.

A great advance towards an interpretation of the mechanism of sensitisation was made by Cario and Franck (*Z. Physik*, **11,** 162, 1922) in their discovery that atomic hydrogen is produced from hydrogen molecules when a mixture of H_2 and mercury vapour is illuminated by light containing the mercury resonance line 2537 Å. In the last few years, other gas reactions sensitised by mercury vapour (including examples not involving hydrogen) have been investigated, and the field appears to be one of increasing significance. The very intimate connection between such photosensitised reactions and experiments on resonance radiation, fluorescence, etc. is of considerable advantage, since we have the possibility of directly applying the fairly well-established interpretation of the physical measurements to the more complex chemical changes. Certain of these reactions may be regarded as the simplest cases of photosensitisation, and we shall therefore discuss first reactions sensitised by mercury vapour.

PHOTOSENSITISATION BY OPTICALLY EXCITED MERCURY VAPOUR.

In Chapter V., we have seen that the addition of other gases (atoms or molecules) to mercury vapour and illumination of the system by the 2537 Å line is accompanied by one or other of the following effects: (*a*) "damping" of the resonance radiation, (*b*) emission of sensitised fluorescence, (*c*) sensitised chemical reaction. Cases (*a*) and (*b*) have already been discussed, as also one example of case (*c*), the dissociation of hydrogen into atoms; we now proceed to consider further reactions sensitised by mercury vapour. Such cases may be divided into two classes according as to whether or not hydrogen is one of the reactants.

Reactions Involving Hydrogen.—Since in these cases hydrogen atoms are formed on illumination of the system with light containing the resonance line 2537 Å, a brief description of the chemical properties of atomic hydrogen is not without interest.* Active hydrogen may be formed (*a*) from molecular hydrogen at high temperatures and low pressures (Langmuir, *J. Amer. Chem. Soc.*, **34,** 860, 1912), (*b*) by the passage of a high tension discharge through moist hydrogen (Wood, *Phil. Mag.*, **43,** 729, 1921; **44,** 538, 1922; *Proc. Roy. Soc.*, **97**A, 455, 1921; **102**A, 1, 1922), and (*c*) by the Franck-Cario method. The substance formed by these methods is almost certainly atomic hydrogen (cf. Herzfeld, *Z. Physik*, **8,** 132, 1922), though certain workers have assumed that the product of method (*b*) is H_3, whose existence has been proved by J. J. Thomson (1913) by the positive ray method. Langmuir demonstrated that glass surfaces strongly adsorb atomic hydrogen, causing the "clean-up" or diminution in pressure of the system with time. He also showed that a number of metallic oxides are reduced by hydrogen atoms at ordinary temperatures, and determined the energy of dissociation of hydrogen molecules to be in the neighbourhood of 80,000 to 100,000 cal. per mole. Bonhoeffer (*Z. physikal. Chem.*, **113,** 199, 1924; **116,** 391, 1925) and Bonhoeffer and Boehm (*ibid.*, **119,** 385, 1926) have studied the chemical properties of hydrogen atoms formed by Wood's method. They found that active hydrogen thus formed reduces at room temperature a number of solid substances such as oxides and sulphides, sulphur, arsenic, and antimony, and also hydrogenates oleic acid. The reaction $H + H \rightarrow H_2$ is catalysed by the glass walls of the containing vessel and by metals, whose catalytic action is in the same order as the order of the metals in the hydrogen overvoltage series. The half-life period of activity under the conditions of Bonhoeffer's experiments was in the neighbourhood of 0·2 sec., from which it appears that only about one collision in 10,000 between hydrogen atoms leads to the formation of molecular hydrogen (compare Chapter VI., p. 341). In studying the reactivity of H atoms with other gases, it was found that oxygen reacts giving a high percentage of H_2O_2, while halogens react to form halogen acids, e.g.

$$H + Cl_2 \rightarrow HCl + Cl$$
$$H + Cl \rightarrow HCl.$$

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* A useful summary of the properties of atomic hydrogen is given by H. S. Taylor, *J. Amer. Chem. Soc.*, 48, 2840, 1926.

(These reactions with chlorine and bromine were also investigated by Marshall (*J. Physical Chem.*, **29,** 842, 1925), who showed that, per H atom, Cl_2 gives a larger yield of halogen acid than does Br_2). CO and CO_2 form small quantities of formaldehyde with hydrogen atoms, the reactions appearing to be much slower than those with the halogens. Active hydrogen is rapidly destroyed by HCl, HBr, H_2S, and CH_3Cl, the mechanisms of these reactions being conjectured to be

$$H + HCl \rightarrow H_2 + Cl, \; Cl + H \rightarrow HCl\,;$$
$$H + H_2S \rightarrow HS + H_2, \; HS + HS \rightarrow H_2 + S_2\,; \text{ etc.}$$

Finally, N_2, H_2O, NH_3, and CH_4 appear to be unacted upon by atomic hydrogen, and Bonhoeffer explains the difference in behaviour between these and the formerly mentioned substances on thermochemical grounds.

Dealing now with sensitised reactions in optically excited mercury vapour, the work of Franck and Cario has been extended by the studies of American investigators, particularly by Taylor, by Marshall, and by Dickinson. We shall not discuss the experimental technique of such work, but only point out that a " cold " mercury arc must be used as a source of light in order to prevent self-absorption of the resonance line 2537 Å. Also it might be noted that in the work of Taylor and Marshall the reacting system was at comparatively high pressures (0·5 to 1·0 atm.), while in that of most other investigators low pressures of the order of a few mm. or less were used.

Preliminary work on a number of mercury-sensitised reactions involving hydrogen was carried out by H. S. Taylor (*Trans. Faraday Soc.*, **21**, 560, 1926). Using the static-manometric method, the effect of illuminating mixtures (containing small amounts of Hg vapour) of H_2 with (1) C_2H_4, (2) CO, (3) O_2, (4) N_2O, (5) CO_2, and (6) N_2 was investigated, and reaction found to occur at room temperature in cases (1) to (4). The rates of reaction were comparatively great; thus, for the reaction between ethylene and hydrogen, a velocity corresponding to a decrease of pressure of the order of 30 mm. per hour was obtained. The products of reaction were in the several cases (1) ethane, (2) formaldehyde and its solid polymers, (3) and (4) water vapour, but later work has since shown that additional products are formed—at least in cases (1) and (3). The rates of reaction were found to be somewhat variable, and this, together with the fact that the quantum yields of the processes appeared to be high, led Taylor to the view that these sensitised reactions are " chain " processes, a view which more recent work by Marshall appears to confirm. Considering these reactions individually, we shall first deal with the mercury-sensitised reaction between hydrogen and oxygen.

The Reaction between H_2 and O_2 Sensitised by Mercury Vapour.—This reaction is undoubtedly a very complex process. It was first studied by Dickinson (*Proc. Nat. Acad. Sci.*, **10,** 409, 1924), who established that at 45° and also at room temperature water formation takes place when the Hg line 2537 Å is present in the activating light. Low total pressures (about 0·2 mm.) were used and the reaction followed manometrically after freezing out the water in liquid air. Taylor (*loc. cit.*) suggested a mechanism for the process, in which the intermediate formation of H_2O_2 was postulated, thus—

$$\begin{aligned}&Hg^* + H_2 \rightarrow Hg + 2H\\&H + O_2 \rightarrow HO_2\\&HO_2 + H_2 \rightarrow H_2O_2 + H\\&H_2O_2 \rightarrow H_2O + O\\&O + H_2 \rightarrow H_2O.\end{aligned}$$

The intermediate formation of H_2O_2 was confirmed by Marshall,† who found that with different experimental conditions H_2O_2 may be practically the only product of reaction. In the experiments described in a first paper (*J. Physical Chem.*, **30,** 34, 1926), however, Marshall employed the static method and endeavoured to find the dependence of the rate of reaction on the concentrations of hydrogen and oxygen. Somewhat non-reproducible results were obtained, but individual experiments appeared to be satisfied best by an equation of the type

$$\frac{d[H_2O]}{dt} = k \cdot \frac{p_{H_2}}{p_{H_2} + p_{O_2}}.$$

Practically all experiments gave a final pressure decrease corresponding to that calculated on the basis of a net reaction $2H_2 + O_2 \rightarrow 2H_2O$, and with stoichiometric mixtures $(2H_2 + O_2)$ linear pressure-time curves were obtained, stopping abruptly at the theoretical end point. Temperatures of 40° to 70° C. were employed ; at the higher temperature, considerable amounts of mercuric oxide were formed, possibly by the action of H_2O_2 vapour on mercury (cf. Elder and Rideal, *Trans. Faraday Soc.*, **23,** 545, 1927). The mechanism postulated for water formation was a " chain " practically identical with that of Taylor. In a second paper (*J. Physical Chem.*, **30,** 1079, 1926) Marshall showed, using a dynamic method, that H_2O_2 is the first isolable product of reaction, and that it may be obtained in large amounts. He also attempted the difficult problem of estimating the quantum efficiency of the process, making measurements of the light absorption during the reaction and determining the H_2O_2 yield. He used a circulatory system, in which the mixture of H_2 and O_2 was saturated with Hg vapour at 50° and then passed through the reaction vessel, maintained at 70° to 80°, into a vessel cooled with liquid air to condense the H_2O_2 formed. The yield of H_2O_2 found was 4·6 molecules per quantum, which, however, must be regarded as a minimum figure. Owing to unavoidable decomposition of H_2O_2 and to other causes, the " true " quantum yield is probably considerably greater, and, if the difficult absorption measurements are reliable, the reaction must be a " chain " process. Marshall also observed that N_2 has practically no influence on the velocity of the sensitised reaction, a result which is in agreement with Stuart's observations (*Z. Physik*, **36,** 262, 1925) on the inefficiency of this gas for deactivating excited mercury atoms.

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† Cf. also Hirst, *Proc. Camb. Phil. Soc.*, **23,** 162, 1926 ; Hirst and Rideal, *Nature*, **116,** 899, 1925.

In further experiments (*J. Amer. Chem. Soc.*, **49,** 2763, 1927) using a streaming method and with an improved type of mercury arc, the rate of hydrogen peroxide formation was found to be given by the equation

$$\frac{d[H_2O_2]}{dt} = k \cdot \frac{p_{H_2}}{p_{H_2} + p_{O_2}},$$

i.e. by the same expression previously found for the rate of *water* formation in a stationary gas mixture. This appears to indicate that under the conditions of the static method the rate of decomposition of H_2O_2 was of the same magnitude as its rate of formation. It was also shown that under favourable conditions of working of the dynamic method, practically all the H_2O_2 formed may be recovered unchanged, that the temperature coefficient of the reaction is nearly unity, and that the optimum concentration of Hg vapour for the reaction is about 0·005 mm. With greater partial pressures of mercury vapour, the increased rate of reaction is more than balanced by increased decomposition of the H_2O_2 formed. The kinetic equation

$$\frac{dx}{dt} = k \cdot \frac{p_{H_2}}{p_{H_2} + p_{O_2}}$$

for the rate of combination of H_2 and O_2 sensitised by mercury vapour is quite different from that of the same reaction sensitised by chlorine (p. 530), which is not a "chain" process. The above equation suggests that the velocity of the mercury-sensitised process is governed essentially by the rate of deactivation of Hg* atoms by hydrogen molecules, which will be approximately proportional to $\frac{p_{H_2}}{p_{H_2} + p_{O_2}}$, since according to the measurements of Stuart (*loc. cit.*) oxygen and hydrogen are about equally efficient in deactivating excited mercury atoms. It appears to be certain, however, that the reaction course is more complex than this, since other work shows that ozone formation takes place in Hg—O_2 mixtures on illumination with 2537 Å line, and therefore a complicated series of processes must occur in Hg—H_2—O_2 mixtures, involving both formation and decomposition of H_2O_2, of O_3, and of H_2O molecules. Evidence that water molecules are decomposed by optically excited mercury vapour has been supplied by Senftleben and Rehren (*Z. Physik*, **37,** 529, 1926). In continuation of previous work (*ibid.*, **32,** 922, 1925) in which it was shown that the thermal conductivity of hydrogen (containing Hg vapour) increases on illumination due to the formation of hydrogen atoms, these workers demonstrated by the same method that water is dissociated by collisions of the second kind with excited mercury. Using low pressures of water vapour, they found that the sole product of reaction non-condensable at the temperature of liquid air was hydrogen.† The absence of oxygen under these conditions may be due either to the net reaction being

$$2H_2O \rightarrow H_2O_2 + H_2$$

or to oxygen reacting with Hg to form HgO. Three possible results of a collision between an excited Hg atom and a water molecule were considered, viz.

$$(1)\ H_2O + 112{,}000 \text{ cal.} \rightarrow H + H + O$$
$$(2)\ H_2O + 112{,}000 \text{ cal.} \rightarrow H_2 + O$$
$$(3)\ H_2O + 112{,}000 \text{ cal.} \rightarrow H + OH.$$

It was concluded that the energy supplied by the activated Hg atom is not sufficient to enable either (1) or (2) to take place, and that consequently (3) must be the process which actually occurs.

Reserving for later discussion the question of possible interactions between O_2 molecules and excited Hg atoms, we have taken the view in the foregoing that the primary step in Hg-sensitised processes involving hydrogen is that represented by the equation

$$H_2 + Hg^* \rightarrow 2H + Hg.$$

Two other possibilities have, however, been suggested, namely (1) the formation of mercury hydride

$$Hg^* + H_2 \rightarrow HgH + H$$

(Compton and Turner, *Phil. Mag.*, **48,** 360, 1924; *Phys. Rev.*, **25,** 606, 1924), and (2) the formation of an activated hydrogen molecule (Dickinson, *Proc. Nat. Acad. Sci.*, **10,** 409, 1924; Mitchell, *ibid.*, **11,** 458, 1925; Rideal and Hirst, *Nature*, **116,** 899, 1925). Compton and Turner found mercury hydride bands in Geissler discharge tubes containing Hg and H_2, the bands being of greatest intensity at the places at which the concentration of Hg atoms in the 2^3P_1 state was greatest, and they suggested that the mode of formation of the hydride was that represented above. The view that hydrogen molecules with high vibrational energy content may be formed results from the work of Mitchell on sensitised water formation, which is briefly discussed below. Actually, we have no means of deciding what the actual primary process is, but it is possible that the three suggested above occur simultaneously. According to Nordheim (*Z. Physik*, **36,** 496, 1926), the most probable result of a collision of the second kind is the one in which least energy is transformed into kinetic energy, and this condition would entail that the most frequent primary process would be the direct dissociation of the hydrogen molecule into atoms.

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† Taylor and Bates (*J. Amer. Chem. Soc.*, **49,** 2438, 1927), *using a flow method*, found that the residual gas consisted of 73 per cent. H_2. 27 per cent. O_2 (by vol.).

The work of Mitchell (*Proc. Nat. Acad. Sci.*, **11,** 458, 1926) on sensitised water formation has been above referred to. Using a static method, experiments were conducted in which mixtures of hydrogen and oxygen and of hydrogen, oxygen, and argon were illuminated at 45° in the presence of saturated mercury vapour. The rate of diminution of the pressure (after removal of condensable gases) was followed; it was found that, with a constant partial pressure of oxygen of 0·036 mm., the velocity of reaction increased with increasing hydrogen content, but appeared to approach a limiting value. With constant partial pressure of H_2 (0·04 mm.), the rate increased with increasing oxygen content, passed through a maximum at $p_{O_2} = 0{\cdot}01$ mm., then decreased to a small constant speed. The most interesting observation made, however, was that, with constant partial pressures of oxygen and hydrogen, addition of argon caused a diminution in reaction rate, and in the presence of sufficient argon ($p_A = 6(p_{H_2} + p_{O_2})$) the velocity of reaction became inappreciable. This result is contrary to what might have been anticipated. Most collisions between Hg (2^3P_1) atoms and argon atoms are elastic, and such collisions as are inelastic do not completely deactivate the mercury atoms but transform them to the long-lived metastable 2^3P_0 state. The Hg (2^3P_0) atom, however, is equally as efficient as the 2^3P_1 atom in exciting H_2 by collision (Meyer, *Z. Physik*, **37,** 639, 1926), while stable with respect to collisions with Hg and with A; it follows, therefore, that in mixtures containing little hydrogen, more energy should be transferred to the latter gas when argon is present than in absence of the inert gas. Several suggestions have been advanced to account for the apparently contradictory result of Mitchell. He himself proposes either that the addition of argon favours the recombination process $2H \rightarrow H_2$ by supplying a molecule (more suitable than H_2) to act as the third particle of the requisite ternary collision, or that the formation of water does not take place *via* hydrogen atoms but *via* strongly vibrating hydrogen molecules. The addition of argon would then diminish the rate of water formation owing to increased deactivation of activated hydrogen molecules by the added argon. Olson and Meyers (*J. Amer. Chem. Soc.*, **48,** 389, 1926) suggest an alternative explanation, retaining the view that hydrogen atoms are the reacting entities. According to them, hydrogen atoms must diffuse from the region of absorption by Hg vapour into the main body of the gas in order that reaction with oxygen may ensue; this diffusion process is retarded by the addition of an indifferent gas. The result of Loria (*Physical Rev.*, **26,** 573, 1925), who found that the sensitised fluorescence of Tl in mercury vapour excited by the 2537 Å line is increased by inert gases, is similarly attributed to a decrease in the rate of diffusion of excited Tl atoms from the region in which they are formed. The re-emission of the energy would then occur mainly at the front of the tube, i.e. nearer the point of observation, with an apparent increase in the intensity of sensitised fluorescence.

We must finally mention the work of Taylor and Bates (*J. Amer.*

Chem. Soc., **49,** 2438, 1927) on the sensitised formation of H_2O_2. Using a flow method in which the mixture of H_2 and O_2 at atmospheric pressure was saturated with mercury vapour at 25° and then passed through the illuminated reaction vessel, large yields of H_2O_2 were obtained. It was found that H_2O_2 was formed only if mercury vapour was present in the insolated gas mixture; on the other hand, ozone was obtained both in presence and in absence of mercury. In their experiments with Hg present, mercuric oxide was formed beyond the illuminated area. Since many molecules of H_2O_2 are formed per Hg atom present (values up to 250 were found), the formation of mercuric oxide is a secondary process, probably due to reaction of H_2O_2 with Hg. The results were not too reproducible, which can be attributed to variations in the amounts of H_2O_2 decomposed photochemically and by reaction with Hg.

The Polymerisation and Hydrogenation of Ethylene.—Berthelot and Gaudechon (*Compt. rend.*, **150,** 1169, 1910), in a study of the effect of ultra-violet light on a number of organic substances, found that ethylene (and acetylene) undergo polymerisation. Mercury vapour was, however, present in their insolated system, and the later work quoted below shows that the ethylene reaction is entirely a mercury-sensitised process. The reactivity of ethylene—either alone or with hydrogen—in presence of optically excited mercury vapour has been investigated by Taylor and Marshall (*J. Physical Chem.*, **29,** 1140, 1925), by Taylor and Bates (*J. Amer. Chem. Soc.*, **49,** 2438, 1927), and by Olson and Meyers (*J. Amer. Chem. Soc.*, **48,** 389, 1926; *ibid.*, **49,** 3131, 1927).

In preliminary work, Taylor and Marshall, using the static method and comparatively high pressures, obtained with equivalent amounts of ethylene and hydrogen, or with excess of the latter, approximately linear pressure-time curves with end points corresponding to those calculated on the assumption that the only reaction occurring is $C_2H_4 + H_2 \rightarrow C_2H_6$. More quantitative measurements were carried out by Olson and Meyers. They used the static-manometric method, the temperature of the reacting system being 45°. In experiments with ethylene alone (initial pressure 0·6 mm.), it was found that on illumination with the cooled arc an increase of pressure occurred at the start, soon followed by a pressure decrease. In no case did the final pressure become zero, as is required for a pure photo-polymerisation, but the final pressure obtained was about equal to the initial increase of pressure. The final products of reaction were solid polymers together with some ethane. The hydrogenation of ethylene was studied at greater total pressures (1 to 12 mm.). In each experiment hydrogen was present in excess, and the final diminution in pressure was equal to the initial pressure of ethylene. In cases in which hydrogen was present in great excess, no solid deposit was observed on the walls of the reaction vessel. In other cases a slight deposit was obtained, and there was also a small change of slope in the pressure-time curves near the start of the reaction, due clearly to the same processes which, in the absence of H_2, produce a maximum point on the curve. According to Olson and Meyers, all their experiments demonstrate that the initial rate of reaction between hydrogen and ethylene is proportional to the square root of the pressure of hydrogen. This result they interpret as follows. Owing to the very high absorption coefficient of mercury vapour for the 2537 Å line, excitation of mercury and formation of hydrogen atoms occur only within a short distance of the place of entry of the activating light. This region is soon denuded of ethylene (by reaction with hydrogen) and further reaction must occur by diffusion of hydrogen atoms into the main body of gas. Olson and Meyers suggest that the velocity measured, i.e. the slowest of a series of processes, is the rate of diffusion of hydrogen atoms. This rate is proportional to the first power of the concentration of H in the absorbing zone, which in turn is proportional to the square root of the concentration of H_2. In continuation of their work, Olson and Meyers carried out further experiments to determine the resultants of the sensitised ethylene-hydrogen reaction more definitely. The reaction products were therefore subjected to analysis by the positive ray method described by Hogness and Lunn (*Physical Rev.*, **26,** 44, 1925), and in two experiments (static method) the following results were obtained:—

Expt.	Initial Compn. (cm. Hg).		Time of Illumination (Hours).	Pressure Decrease (cm. Hg).	Final Compn. (cm. Hg).				
	H_2.	C_2H_4.			CH_4.	C_2H_6.	C_3H_8.	C_4H_{10}.	H_2.
I	39	25	39	24	0·16	8·9	5·8	3·75	21
II	40	2	50	2	0·376	1·71	0·068	0·0013	38

These results, together with those of their previous work, led Olson and Meyers to formulate the following reaction mechanism. Three primary processes are considered probable, namely,

(1) $Hg^* + H_2 \rightarrow Hg + 2H$,
(2) a splitting off of hydrogen from ethylene by collision with Hg^* (for example, $C_2H_4 + Hg^* \rightarrow C_2H_2 + H_2 + Hg$), and
(3) $C_2H_4 + Hg^* \rightarrow 2CH_2 + Hg$.

The introduction of the last of these reactions is necessitated by the appearance of methane as a reaction product. Given these primary processes, the following secondary processes may be considered:—

(4) $C_2H_4 + 2H \rightarrow C_2H_6$
(5) $CH_2 + 2H \rightarrow CH_4$
(6) $CH_2 + C_2H_4 + 2H \rightarrow C_3H_8$
(7) $2CH_2 + C_2H_4 + 2H \rightarrow C_4H_{10}$
(8) $C_2H_4 + C_2H_x + yH \rightarrow C_4H_{10}$

(C_2H_x is the resultant of primary process (2)). Assuming that the amount of CH_2 formed (reaction (3)) is proportional to the ethylene concentration, Olson and Meyers conclude, on the basis of the relative yields of the products in the two experiments, that reaction (7) does not take place to an appreciable extent. This is not in disagreement with the fact that longer chain hydrocarbons than butane are absent. The mechanism proposed is one that accounts well for the variations in relative yields of methane, propane, and butane in mixtures of varying ratio $C_2H_4 : H_2$.

The results of Taylor and Bates are in general agreement with those of the first paper of Olson and Meyers. Using a static method and mixtures of ethylene and hydrogen at atmospheric pressure, they found that the reaction rate (as measured by the fall in pressure) was approximately constant for the major portion of an experiment, though the initial velocity was somewhat less and a rapid decrease in rate occurred towards the end. The final diminution in pressure was, in all cases, greater than the initial partial pressure of ethylene. This "over-running" of the reaction beyond the end point predicted on the assumption that the change is solely $C_2H_4 + H_2 \rightarrow C_2H_6$ was attributed to polymerisation of ethylene. Investigation of the reactivity of ethylene (in absence of hydrogen) in the presence of optically excited mercury vapour gave results agreeing with those of Olson and Meyers. In addition to solid polymerisation products, the gaseous products contained acetylene and hydrogen, which were detected in separate experiments using a flow method. Indications were also obtained that other hydrocarbons were present, though in insufficient amount to be identified. In contrast to ethylene which is unaffected by ultra-violet light when Hg vapour is absent, acetylene polymerises (to form solid cuprene) both by direct photochemical action and by a mercury-sensitised process.

On the basis of these facts, the following mechanism for the sensitised decomposition and polymerisation of ethylene was proposed, to which is appended the reaction scheme previously suggested by Taylor (*Trans. Faraday Soc.*, **21**, 560, 1926) for the hydrogenation reaction. Two primary processes are assumed (both C_2H_4 and H_2 being present)—

$$(1)\ C_2H_4 + Hg^* \rightarrow C_2H_2 + H_2 + Hg$$
$$(2)\ H_2 + Hg^* \rightarrow 2H + Hg.$$

The hydrogenation reaction is presumed to be a "chain" process, occurring *via* the production of free ethyl radicals, thus—

$$\left.\begin{array}{l}(3)\ C_2H_4 + H \rightarrow C_2H_5\\ (4)\ C_2H_5 + H_2 \rightarrow C_2H_6 + H\end{array}\right\}\text{chain.}$$

Using a somewhat uncertain value of the energy of the C = C linkage, it is calculated that both processes (3) and (4) are exothermic, and thus a "chain" of the above type is at least plausible.†

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† Bonhoeffer and Harteck (*Z. physikal. Chem.*, **139**, 64, 1928) point out that the first stage in Taylor's mechanism is an association process and thus

Polymerisation might occur by reaction of the C_2H_2 formed in (1) in the following manner:—

(5) $C_2H_2 + Hg^* \rightarrow C_2H_2^*$, (6) $C_2H_2^* + (n - 1)C_2H_2 \rightarrow (C_2H_2)_n$;

or

(5*a*) $C_2H_2 + h\nu \rightarrow C_2H_2^a$, (6*a*) $C_2H_2^a + (n - 1)C_2H_2 \rightarrow (C_2H_2)_n$.

Again, we have the possibility of reaction between hydrogen atoms and the products of reactions (6) and (6*a*), as well as addition reactions between C_2H_5 radicals and ethylene. It will be noticed that while this mechanism concentrates on the possible modes of formation of solid polymers, that of Olson and Meyers—in which an extra primary process is assumed—is concerned rather with reactions which might lead to the formation of saturated hydrocarbons (other than ethane). The results of both investigations make clear, however, the complex nature of the reactions which occur in this sensitised process.

Photosensitised Reactions between Carbon Monoxide (and Carbon Dioxide) and Hydrogen.—Marshall and Taylor (*J. Physical Chem.*, **29,** 1140, 1925) showed that in the presence of optically excited mercury vapour, CO and H_2 react with formation of formaldehyde and of solid polymerisation products, together with some methane. Formaldehyde was considered to be the primary product of reaction and it was suggested that hydrogen atoms reacted with normal CO molecules, non-activation of the latter being inferred from the fact that no reaction between CO and O_2 could be detected in the presence of excited mercury vapour. The rate of reaction between CO and H_2 was comparatively rapid under Marshall and Taylor's experimental conditions; on the other hand, they could detect no reaction between CO_2 and H_2, either with the damp or with the dried gases.

The quantum yield of the reaction $H_2 + CO + Hg^* \rightarrow H.CHO + Hg$ was determined by Marshall (*J. Physical Chem.*, **30,** 1078, 1926). Using the same methods as in the case of the H_2—O_2 reaction, the highest quantum yield experimentally determined was 6, the value being calculated on the basis of the rate of decrease of pressure.† As in the H_2—O_2 reaction, this quantum yield is to be regarded as less than the true value. It was found that the rate of reaction steadily decreased as the reaction proceeded, and that the two reactants disappeared in a 1 : 1 ratio. In further work (Marshall, *J. Physical Chem.*, **30,** 1634, 1926), attempts were made to elucidate the kinetics of this photosensitised reaction. A circulatory system was employed, the gases being saturated with mercury at 80°, the reaction proceeding at 50°, the products condensed in liquid air, and the decrease in pressure measured. As in the H_2—O_2 reaction, great difficulty was experienced

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in the gas phase should require a ternary collision. They therefore suggest that hydrogenation of unsaturated bodies by atomic hydrogen occurs mainly on the walls.

† Other experiments showed that the main product of reaction is formaldehyde or a polymer which readily yields formaldehyde on heating. In one case, the amount of formaldehyde thus obtained was as much as 77 per cent. of that calculated from the decrease of pressure.

in obtaining reproducible results, but comparison of the *initial* rates of reaction in mixtures of varying composition led Marshall to the view that the velocity is best expressed by the equation

$$\frac{dx}{dt} = k \cdot p_{H_2}^{\frac{1}{2}} \cdot p_{CO} \quad . \quad . \quad . \quad . \quad (1)$$

A mechanism

$$Hg^* + H_2 \rightarrow Hg + 2H$$
$$H + CO \rightarrow HCO$$
$$HCO + H_2 \rightarrow HCHO + H$$
$$H + H \rightarrow H_2$$

leads to the equation

$$\frac{dx}{dt} = k' \cdot p_{H_2}^{\frac{1}{2}} \cdot p_{CO} \cdot \sqrt{\frac{1}{p_{H_2} + p_{CO}}} \quad . \quad . \quad . \quad (2)$$

but tests appeared to indicate that equation (1) rather than (2) applies. Further work is necessary, however, before the kinetics of the reaction can be regarded as satisfactorily settled.

We have seen that Bonhoeffer and Boehm (*Z. physikal. Chem.*, **119**, 385, 1926), in their study of the reactions of atomic hydrogen, found that both CO and CO_2 react to give formaldehyde, whereas Taylor and Marshall (*loc. cit.*) observed a mercury-sensitised reaction between CO and H_2, but none between CO_2 and H_2. The latter was re-investigated by Marshall, who showed that reaction does take place, but at a speed only about 2 per cent. of that of the CO—H_2 reaction under similar conditions. CO and oxygenated organic compound are among the products of reaction.

Other Mercury-Sensitised Reactions Involving Hydrogen.—Two cases only need be mentioned. The first—the reaction between nitrous oxide and hydrogen—was noted by Taylor and Marshall (*J. Physical Chem.*, **29**, 1140, 1925), who found that mixtures of N_2O and H_2 reacted more rapidly than did mixtures of hydrogen and oxygen under similar conditions. Water is one of the reaction products, but, as in the ethylene-hydrogen reaction, the process is complicated by the fact that the "acceptor" for hydrogen atoms (N_2O in this case) is simultaneously decomposed by activated mercury atoms. The second case is that of nitrogen-hydrogen mixtures, which is of interest since conflicting evidence regarding the possibility of ammonia formation has been obtained by different workers. Positive results have been obtained by Hirst (*Proc Camb. Phil. Soc.*, **23**, 162, 1926) and by W. A. Noyes, Jr. (*J. Amer. Chem. Soc.*, **47**, 1003, 1925). The former detected ammonia and traces of hydrazine on illuminating N_2 and H_2 with ultra-violet light in the presence of liquid mercury; the latter obtained ammonia under similar conditions but at the temperature of boiling mercury and at pressures greater than atmospheric. On the other hand, Taylor (*Trans. Faraday Soc.*, **21**, 560, 1925; *J. Amer. Chem. Soc.*, **48**, 2840, 1926) could not detect any ammonia formation in N_2—H_2 mixtures even with intense sources of the resonance radiation, and suggested that Hirst's positive reaction for hydrazine might be due to formaldehyde formed from CO present in the hydrogen. As already mentioned, Bonhoeffer (*Z. physikal. Chem.*, **119,** 385, 1926) found that atomic hydrogen formed by Wood's method gave no detectable amount of ammonia on being led into nitrogen. Yet Willey and Rideal (*J.C.S.*, p. 671, 1927) found evidence for ammonia formation under the same conditions. The evidence for the production of ammonia has been reviewed by B. Lewis (*J. Amer. Chem. Soc.*, **50,** 27, 1928), who concludes on the basis of his own and other work that no ammonia is formed from atomic hydrogen and unexcited molecular nitrogen or from active nitrogen and molecular hydrogen, but that activation of both the reactants is necessary. Whether such simultaneous activation is possible by excited mercury atoms is doubtful; the positive result obtained by Hirst might be ascribed to the presence of a liquid mercury surface and liberation of electrons therefrom.

Mercury-Sensitised Reactions not Involving Hydrogen.—The chief processes to be considered in this connection are a number of photosensitised decompositions and the reactions of oxygen in presence of illuminated mercury vapour. We have already seen that ethylene and water are among the substances which undergo decomposition in presence of optically excited mercury; other cases have been investigated, of which the most prominent is that of ammonia. That a mercury-sensitised decomposition of this substance takes place was demonstrated by Dickinson and Mitchell (*Proc. Nat. Acad. Sci.*, **12,** 692, 1926) and by Taylor and Bates (*ibid.*, **12,** 714, 1926). The former worked with ammonia at low pressures. After illumination, the condensable substances were removed by application of liquid air to a trap, and the pressure and composition of the residual gas determined by the Haber-Kerschbaum quartz-fibre manometer. Both the sensitised reaction and the direct photo-reaction were separately studied, the former by using a cooled and deflected arc and filtering off all light of wave-length below 234 $\mu\mu$, and the latter by employment of the hot arc and no filter. It was found that in the direct photochemical decomposition the mole fraction of hydrogen in the residual gases was 0·87 instead of 0·75, the figure to be anticipated assuming that the reaction is $2NH_3 \rightarrow N_2 + 3H_2$. The difference may be due to hydrazine formation, yet this could not be decided with certainty since the quartz tube liberated some gas on illumination with unfiltered radiation from the mercury lamp. In the sensitised reaction, the average mole fraction of hydrogen in the gaseous resultants was 0·699; the smaller yield than the theoretical is perhaps due to a "clean-up" of hydrogen on the walls. Bates and Taylor (*loc. cit.;* also *J. Amer. Chem. Soc.*, **49,** 2438, 1927) used a flow method with an arc surrounding their reaction vessel, and also determined the products of both sensitised and non-sensitised reactions. They found that the non-condensable gas consisted of 96 per cent. H_2, 4 per cent. N_2 in the direct reaction, and of 89 per cent. H_2, 11 per cent. N_2 in the photosensitised process. They attribute the excess of hydrogen over stoichiometric proportions to hydrazine formation, in agreement with Mitchell and Dickinson. The differences between the results of the two investigations are probably due to differences in experimental method and possibly to differences in pressure.

The effect of added gases on the velocity of the sensitised reaction has been studied by Mitchell and Dickinson (*J. Amer. Chem. Soc.*, **49,** 1478, 1927). Employing the static method, they found that addition of argon or of nitrogen at pressures of 0·3 mm. to ammonia at 3 mm. pressure had no influence on the velocity of the mercury-sensitised decomposition. On the other hand, hydrogen at 0·3 mm. pressure or less was found to exert a very strong inhibitory effect; since hydrogen is formed during the reaction, it follows naturally that the velocity of the process (starting with pure ammonia) decreases markedly as the reaction progresses. It was finally demonstrated that the initial rate of reaction in pure ammonia increases with increasing pressure.

The absence of any effect produced by small additions of nitrogen or of argon and the large effect produced by hydrogen are in general accord with the work of Stuart (cf. p. 276), who found that the intensity of resonance radiation of mercury vapour was reduced to half by 0·2 mm. of hydrogen, 30 mm. of nitrogen, and 240 mm. of argon. The efficiency of hydrogen in diminishing the rate of ammonia decomposition is naturally attributable to the fact that hydrogen as well as ammonia molecules are activated by excited mercury atoms. It might therefore be anticipated that with low pressures of ammonia the pressure of hydrogen necessary to diminish the rate of reaction to one half of the original value would be 0·2 mm. Experiment shows, however, that smaller partial pressures of hydrogen are sufficient to effect this reduction in rate. This may be interpreted, in agreement with Mitchell and Dickinson, by assuming that hydrogen may also deactivate activated ammonia molecules.† These investigators suggest the following mechanism of reaction:—

(0) $Hg + h\nu \rightarrow Hg^*$
(1) $Hg^* + NH_3 \rightarrow Hg + NH_3^*$
(2) $Hg^* + H_2 \rightarrow Hg + H_2^*(2H)$
(3) $Hg^* \rightarrow Hg + h\nu$
(4) $NH_3^* + NH_3 \rightarrow$ resultants
(5) $NH_3^* + H_2 \rightarrow NH_3 + H_2^*(2H)$.

This gives for the rate of reaction

$$\frac{dx}{dt} = \frac{k_1 k_4 K [NH_3]^2}{\{k_1[NH_3] + k_2[H_2] + k_3\}\{k_4[NH_3] + k_5[H_2]\}},$$

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† This assumption was also made by Kuhn (cf. p. 470) to account for the retardation of the direct photochemical decomposition of ammonia by hydrogen at high temperatures.

in which K is the constant rate of formation of activated mercury atoms. This equation, in which the two terms of the denominator clearly display the dual inhibitory nature of the part played by hydrogen, is not in disagreement with the experimental data. On the basis of this mechanism and from experiments in which the initial rates of reaction were determined with different pressures of ammonia, Mitchell and Dickinson calculated the ratio k_1/k_3. Knowing this and also the ratio k_2/k_3 from the work of Stuart, they find that $k_1/k_2 = 0{\cdot}04$, i.e. the specific rate of deactivation of excited mercury by ammonia is but 0·04 of the specific rate of deactivation by hydrogen.

It is of interest to compare the sensitised decomposition of ammonia with the direct decomposition by ultra-violet light (cf. p. 468). We have seen that in the latter process hydrogen has no retarding effect at ordinary temperatures (Warburg), but inhibition by hydrogen occurs at high temperatures (Kuhn). On the other hand, nitrogen is without influence either on the sensitised or on the non-sensitised reaction. In Chapter VIII. we have criticised the mechanism suggested by Kuhn for the direct reaction ; the same mechanism has also been adversely dealt with by Taylor and Bates (*loc. cit.*), who put forward an alternative theory which presumably applies in its main outlines to both sensitised and direct decompositions. Bates and Taylor believe that every activated molecule of ammonia reacts ; the contrary suggestion of Kuhn, that the low quantum yields of the direct photolysis are due to loss of energy on the part of activated NH_3 molecules by re-emission of radiation, seems to be negatived by the fact that the quantum yield is independent of the pressure of ammonia. On the basis of their own and Kuhn's experimental work, they propose the mechanism represented by the following equations :—

$$\begin{aligned}
&(1)\ NH_3 + h\nu \rightarrow NH_3^*\\
&(2)\ NH_3^* + NH_3 \rightarrow N_2H_4 + H_2\\
&(3)\ NH_3^* \rightarrow NH_2 + H\\
&(4)\ NH_2 + NH_3 \rightarrow N_2H_4 + H\\
&(5)\ NH_2 + H_2 \rightarrow NH_3 + H.
\end{aligned}$$

These reactions result in little or no change in pressure and thus would not be measurable in Kuhn's or Warburg's experiments as quantum yields. The reaction which is measured according to the theory of Taylor and Bates is the decomposition of hydrazine, which might take place either thermally or photochemically. The remarkable result found by Kuhn, that the quantum yield decreases on improving the monochromatism of the activating light, is attributed to inability of hydrazine to absorb "monochromatic" light of $\lambda = 206{\cdot}3\ \mu\mu$, while it is able to absorb somewhere in the region 202·5–214·0 $\mu\mu$. Further, Taylor and Bates suggest that the variation in quantum yield with temperature is due to reversal of process (4) at low temperatures, such reversal being less probable at high temperatures on account of (*a*) the greater rate of thermal decompositions of hydrazine and (*b*) more rapid recombination of hydrogen atoms. As these authors point out, however, this mechanism does *not* account for the fact that no inhibition by hydrogen occurs at low temperatures, and thus it cannot be deemed satisfactory in its present form. Although as yet the formation of hydrazine in either the sensitised or non-sensitised reaction has not been established with absolute certainty, it is probable that this gas is an intermediate (and also final) product of reaction, and accordingly the theory of Taylor and Bates appears certainly to be an advance on that of Kuhn.

A number of other mercury-sensitised decompositions have also been studied by Taylor and Bates (*loc. cit.*). It was found that water, ammonia, ethylene, methyl alcohol, ethyl alcohol, benzene, acetone, formic acid, and ethylamine were all decomposed in the presence of optically excited mercury vapour, and the products of decomposition non-condensable in liquid air were determined. A dynamic method was used, the vapour of the substance being saturated with mercury vapour at 50° and passed through the illuminated reaction vessel into liquid air traps. The pressure of the issuing gas was measured on a McLeod gauge, and the gases subjected to analysis. A similar procedure was adopted with all mercury carefully removed from the apparatus, in order to compare the rates of the sensitised and the non-sensitised reactions. Table LII. summarises the results obtained. It will be observed that in each case, under the experimental conditions employed, the sensitised reaction is faster than the non-sensitised, and in most cases very considerably so. The first three reactions in the table have already been discussed; presumably they are the simplest. Regarding the others, it was noticed that the decompositions of methyl and ethyl alcohols proceed *via* the intermediate formation of aldehydes, which substances were detected in the liquid air traps. In the case of benzene, though the pressure of the non-condensable gases was the lowest obtained, this does not necessarily mean that the process is the least efficient, since much solid (a tarry product containing diphenyl) was simultaneously produced. The relatively large amount of CH_4 present (40 per cent.) in the residual gases makes it likely that, in addition to a dehydrogenation reaction $C_6H_6 + Hg^* \rightarrow C_6H_5 + H + Hg$, the excited mercury atom also disrupts the benzene molecule. The decomposition of formic acid is of interest. The thermal decomposition is a heterogeneous reaction and has been studied on a variety of surfaces by Hinshelwood and Topley (*J.C.S.*, **123,** 1014, 1923). The process takes place in two ways :—

$$(1)\ HCOOH \rightarrow H_2O + CO$$
$$(2)\ HCOOH \rightarrow H_2 + CO_2.$$

The direct photochemical decomposition has been investigated by Ramsperger and Porter (*J. Amer. Chem. Soc.*, **48,** 1267, 1926), who found that on complete decomposition of formic acid vapour at 20° in ultra-violet light, 64 per cent. of the decomposition occurred according to (1). Taylor and Bates' results for the mercury-sensitised reaction show that 76 per cent. of the decomposition takes place

TABLE LII.

COMPARISON OF PHOTOCHEMICAL AND MERCURY-SENSITISED PHOTOLYSES (TAYLOR AND BATES).

Substance.	Photochemical Decomposition (Hg absent).		Mercury-Sensitised Decomposition.		Ratio of Photo-sensitised Rate to Photo-chemical Rate.
	Residual Gas (mm.).	Composition of Residual Gas.	Residual Gas (mm.).	Composition of Residual Gas.	
H_2O	None	—	1·2	H_2 73 per cent.; O_2 27 per cent.	—
NH_3	0·04	H_2 96 per cent.; N_2 4 per cent.	7·8	H_2 89 per cent.; N_2 11 per cent.	200 : 1
C_2H_4	None	—	24·1	H_2 88 per cent.; CH_4, etc. 12 per cent.	—
CH_3OH	0·03	—	18·0	H_2 58 per cent.; $CH_4 + CO$ 42 per cent.	600 : 1
C_2H_5OH	0·7	—	38·0	H_2 46 per cent.; $CH_4 + CO$ 54 per cent.	50 : 1
C_6H_{14}	0·016	—	17·0	H_2 96 per cent.; CH_4 4 per cent.	1000 : 1
C_6H_6	0·01	—	0·3	H_2 60 per cent.; CH_4 40 per cent.	30 : 1
$(CH_3)_2CO$	4·7	$CO + CH_4$; 100 per cent.	9·6	$CO + CH_4$ 100 per cent.	2 : 1
$H . COOH$	0·06	—	24·4	CO 76 per cent.; H_2 24 per cent.	400 : 1
$C_2H_5 . NH_2$	0·34	N_2 4 per cent.; H_2 96 per cent.	20·4	H_2 96 per cent.; CH_4 3·7 per cent.; N_2 0·3 per cent.	60 : 1

according to (1), 24 per cent. according to (2), and also that the photochemical decomposition is very slow compared to the mercury-sensitised process. It would seem, therefore, that formic acid molecules may decompose in two ways on collision with activated mercury atoms.

The only other mercury-sensitised process which remains to be discussed is the reaction between oxygen and mercury vapour. Dickinson and Sherrill (*Proc. Nat. Acad. Sci.*, **12,** 175, 1926) saturated pure oxygen with mercury and passed the resulting gas through an insolated quartz vessel into a solution of KI. With this arrangement, using light filtered through a solution of tartaric acid (1·7 per cent.), ozone was detected in the issuing gas. (When mercury vapour was absent, however, no ozone could be detected.) The yield of ozone could be increased by taking steps to prevent the ozone first formed from being afterwards photochemically decomposed. It was found that at least 7 molecules of ozone were formed for each Hg atom used (i.e. the ratio of ozone molecules formed to mercury atoms present was 7). The first step in the reaction can thus hardly be

$$Hg^* + O_2 \rightarrow HgO + O.$$

The simplest explanation would appear to be that represented by

$$\begin{gathered} Hg^* + O_2 \rightarrow Hg + O_2^* \\ O_2^* + O_2 \rightarrow O_3 + O, \text{ etc.} \end{gathered}$$

The reactivity of oxygen in presence of optically excited mercury vapour has also been studied by W. A. Noyes, Jr. (*J. Amer. Chem. Soc.*, **49,** 3100, 1927). A static method was employed, with oxygen at partial pressures of about 0·2 mm., and the diminution in pressure due to formation of mercuric oxide was measured. The data obtained indicated that the measured process is to be interpreted as a reaction between ozone and mercury vapour, but it was not possible to explain the results by assuming that ozone was formed by both sensitised and non-sensitised reactions and that the effects were additive. Noyes suggested as the most plausible explanation of his results the formation of a complex between Hg^* and O_2 (HgO_2) which could form ozone on collision with oxygen molecules.

SENSITISATION BY THE HALOGENS.

The importance of the halogens from a photochemical standpoint depends not only on the numerous photo-processes in which they are reactants but also on the processes in which they act as sensitisers. Thus, chlorine sensitises the following gaseous reactions: the combination of H_2 and O_2, of SO_2 and O_2, and of CO and O_2, the decomposition of $COCl_2$ (at high temperatures), of Cl_2O, of SO_2Cl_2, and of ozone. Bromine and iodine are also efficient sensitisers of certain reactions in gaseous and liquid systems. We have discussed many of these processes in previous Chapters; the most important gas reaction left for treatment is the decomposition of ozone sensitised by chlorine and by bromine.

The Sensitised Decomposition of Ozone.—Weigert (*Z. Elektrochem.*, **14,** 591, 1908) found that when mixtures of ozonised oxygen and chlorine are illuminated by violet light, which is absorbed by chlorine but not appreciably by ozone, the latter gas undergoes decomposition. The rate of the sensitised reaction depends entirely on the rate of absorption of energy by the chlorine, and is independent of the concentration of ozone between very wide limits. The chlorine is unchanged at the end of the process, i.e. no permanent formation of an oxide of chlorine results. Weigert's results were confirmed by Bonhoeffer (*Z. Physik.*, **13,** 94, 1923), who also demonstrated that with light of wave-length 406-436 $\mu\mu$ two molecules of ozone decompose per quantum absorbed by the chlorine. The reaction, in respect of ozone, is of zero order, the velocity remaining constant, so far as can be determined, down to very low partial pressures of ozone, certainly down to 0·5 mm. Hg. It is this fact which is so remarkable and which demands an interpretation. Bonhoeffer (*loc. cit.*) also studied the bromine-sensitised decomposition of ozone (using light of the same wave-length). The reaction course is similar to that in the presence of chlorine but has a considerably greater quantum efficiency, about 30 molecules of ozone disappearing per quantum absorbed.

The chlorine-sensitised reaction has aroused considerable discussion, but its mechanism still remains unsettled. Bonhoeffer assumed the primary formation of activated chlorine molecules which could then transfer their excess energy to ozone molecules, the mechanism of reaction being one of the following:—

(1) $Cl_2 + h\nu \rightarrow Cl_2^*$; (2) $Cl_2^* + O_3 \rightarrow Cl_2 + O_3^*$; (3) $O_3^* + O_3 \rightarrow 3O_2$:
or (2) $Cl_2^* + O_3 \rightarrow Cl_2 + O_2 + O$; (3) $O + O_3 \rightarrow 2O_2$;
or (2) $Cl_2^* + O_3 \rightarrow Cl_2O_3^*$; (3) $Cl_2O_3^* + O_3 \rightarrow Cl_2 + 3O_2$.

All these require that activated chlorine molecules should possess an unusually long life, greater than 10^{-7} sec., if the reaction velocity is to be maintained when the ozone concentration of the system is small, and also require that, in spite of their many collisions with electronegative O_2 and Cl_2 molecules, activated Cl_2 molecules still retain sufficient energy to activate ozone molecules. It is clear that the second of these consequences is a proposition tenable with difficulty. Not only is the presumed difference in specific effects of O_2 and O_3 on Cl_2^* molecules much greater than one would anticipate, but also oxygen retardation of many photochemical reactions of chlorine seems to call for strong deactivation of Cl_2^* by O_2, if the activated molecule theory of primary light action be accepted. Allmand (*Trans. Faraday Soc.*, **21,** 603, 1926) has therefore suggested an alternative mechanism which still permits of the reaction being zero-molecular with respect to O_3, but which allows of deactivation by O_2 molecules. This may be written

(1) $Cl_2 + h\nu \rightarrow Cl_2^*$; (2) $Cl_2^* + O_3 \rightarrow Cl_2 + O_3^*$; (3) $Cl_2^* + O_2 \rightarrow Cl_2 + O_2^*$; (4) $O_2^* + O_3 \rightarrow O_2 + O_3^*$; (5) $Cl_2^* \rightarrow Cl_2$; (6) $O_2^* \rightarrow O_2$.

Assuming that k_5 and k_6 are both small, i.e. that the lives of activated Cl_2 and O_2 are long compared with the average times required for these molecules to encounter an ozone molecule, this mechanism yields

$$+\frac{d[O_3{}^*]}{dt} = k_1 I_0 [Cl_2]$$

for the rate of activation of ozone molecules. The mechanism of deozonisation itself is uncertain; it may proceed *via* oxygen atoms, thus

$$O_3{}^* \rightarrow O_2 + O$$
$$O + O_3 \rightarrow 2O_2,$$

or more probably by reaction between non-activated and activated molecules

$$O_3{}^* + O_3 \rightarrow 3O_2.$$

Assuming that every activated molecule succeeds in reacting, the quantum efficiency of the whole process would be two, as is experimentally found.

Weigert's theory of "isochromatic fluorescence" (*Z. physikal. Chem.*, **106**, 407, 1923) is essentially different. He regards the ozone-chlorine reaction as the simplest photo-reaction in which chlorine participates, all the energy absorbed being transformed into chemical energy, even when the ozone concentration is reduced to 0·1 per cent. On the other hand, when chlorine containing moisture or other impurities is illuminated, the absorbed energy is converted into heat (Budde effect). These two modes of transformation are, according to Weigert, analogous to certain of those which may occur in mercury vapour on illumination. In the latter we may have (1) resonance radiation, or (2) conversion of absorbed energy into heat, as when oxygen is added, or (3) conversion of absorbed energy into chemical energy, as when hydrogen is present. Weigert completes the analogy between the two cases by supposing that pure dry chlorine when illuminated emits an "isochromatic fluorescence"—the analogue of resonance in Hg vapour. Again, he compares the pressures of sensitiser and reactant in the Franck-Cario reaction ($p_{Hg} = 0{\cdot}009$ mm., $p_{H_2} = 10$ mm.) with those in the ozone-chlorine reaction ($p_{Cl_2} = 380$ mm., $p_{O_3} = 0{\cdot}5$ mm.), taking for the pressure of reactant the limiting pressure above which all the absorbed energy is chemically utilised. The ratio of reactant to sensitising molecules is very different in the two cases; for the Hg—H_2 reaction $\frac{n_r}{n_s} = 1{\cdot}1 \times 10^3$, for the O_3—Cl_2 case $\frac{n_r}{n_s} = 1{\cdot}3 \times 10^{-3}$. Owing to the much greater absorptive power of Hg vapour, however, one should rather compare volumes in which the incident radiation is reduced to the same extent, and if this is done the number of reacting molecules in each case is about the same. Weigert suggests, therefore, that in the O_3—Cl_2 reaction the light "absorbed" by chlorine molecules is re-emitted, this absorption and emission continues until absorption by an "optically-coupled" complex $Cl_2—O_3$ takes place, when deozonisation results. While the theory is of interest, it should be noted that it has no real experimental support, tests for the detection of the postulated fluorescence having so far yielded negative results.

The foregoing theories all presume formation of activated molecules as the primary process; it is pertinent to enquire whether the kinetics and quantum yield of the reaction cannot be interpreted on the basis of dissociation of chlorine into atoms as primary process. This is indeed the case, but the mechanisms which suggest themselves do not appear such as to gain acceptance. Thus, assuming that there is no difference in chemical reactivity between the activated and non-activated chlorine atoms resulting from the primary action of light, we might postulate the following :—

$$(a)\ Cl_2 + h\nu \rightarrow 2Cl;\quad (b)\ Cl + O_3 \rightarrow ClO_3;\quad (c)\ 2ClO_3 \rightarrow Cl_2 + 3O_2$$

which clearly leads to the correct result, but in which several plausible reaction possibilities are omitted. Thus, if we add the reaction (*d*) $ClO_3 + O_3 \rightarrow Cl + 3O_2$, the quantum yield predicted attains values greater than 2, and the reaction rate becomes dependent on the ozone concentration. We could, however, alter reaction (*d*) to $ClO_3 + O_3 \rightarrow Cl + 2O_3$, correct results again being obtained. Yet there appears to be no reason why reaction (*c*) should not be (*c′*) $2ClO_3 \rightarrow Cl_2O_6$, an oxide of this constitution having recently been isolated (see p. 605). The mechanism is hardly acceptable in its present form. Cathala (*J. Chim. phys.*, **25,** 182, 1928) suggests one of the following :—

A.

(1) $Cl_2 + h\nu \rightarrow Cl + Cl$
(2) $Cl + Cl_2 \rightarrow Cl_3$
(3) $Cl_3 + O_3 \rightarrow Cl_2O + ClO_2$
(4) $Cl_2O + O_3 \rightarrow Cl_2 + 2O_2$
(5) $ClO_2 + Cl \rightarrow Cl_2 + O_2$.

B.

(1) $Cl_2 + h\nu \rightarrow 2Cl$
(2) $Cl + O_2 \rightarrow ClO_2$
(3) $Cl + Cl_2 \rightarrow Cl_3$
(4) $ClO_2 + Cl_3 \rightarrow 2Cl_2O$
(5) $Cl_2O + O_3 \rightarrow Cl_2 + 2O_2$.

Both these apparently lead to the correct result, but examination shows that in each a fallacy is contained, and it is perhaps instructive to show where the fallacy lies. Thus, considering mechanism B and obtaining expressions for the stationary concentrations of the intermediate products in the usual way, we (apparently) obtain

$$[Cl] = \frac{2k_1I_0[Cl_2]}{k_2[O_2] + k_3[Cl_2]}$$

$$[Cl_3] = \frac{k_3[Cl][Cl_2]}{k_4[ClO_2]}$$

$$[ClO_2] = \frac{k_2[Cl][O_2]}{k_4[Cl_3]}$$

$$[Cl_2O] = \frac{2k_4[Cl_3][ClO_2]}{k_5[O_3]}.$$

Hence $$k_2[O_2] = k_3[Cl_2]$$

and $$-\frac{d[O_3]}{dt} = k_5[Cl_2O][O_3]$$
$$= 2k_4[Cl_3][ClO_2]$$
$$= 2k_2[Cl][O_2]$$
$$= \frac{4k_1k_2I_0[Cl_2][O_2]}{k_2[O_2] + k_3[Cl_2]}$$
$$= 2k_1I_0[Cl_2].$$

But it is seen from (4) that ClO_2 and Cl_3 necessarily *disappear* at the same rate, and hence, if (as assumed above) stationary state concentrations of these substances are to be maintained, they must also be *formed* at the same rate, i.e. the velocity of (2) is equal to that of (3). But there is no *a priori* reason why the actual rate of combination of Cl atoms with Cl_2 is the same as that with O_2, and it is clear that if it so happens that they are identical under one set of experimental conditions, they will not be so with a different $Cl_2 : O_2$ ratio. It follows, therefore, that stationary state conditions cannot apply for one or other of the substances Cl_3 and ClO_2, i.e. one of them should be steadily built up as the reaction proceeds. A similar misapprehension is inherent in mechanism A, as may easily be shown.

Turning to the Franck mechanism for the primary action of light on chlorine, namely, dissociation into an activated and a non-activated atom, and assuming, as was done by Cremer (p. 555) for the hydrogen-chlorine reaction, that only the activated atom enters into reaction, we may perhaps arrive at the correct result, but again the scheme is not inherently very plausible. Thus the assumption of

$$Cl_2 + h\nu \rightarrow Cl^* + Cl$$
$$Cl^* + Cl_2 \rightarrow Cl_3^*$$
$$Cl^* + O_2 \rightarrow Cl + O_2^*$$
$$Cl_3^* + O_2 \rightarrow Cl_2 + Cl + O_2^*$$

(all these being reactions postulated by Cremer), together with

$$O_2^* + O_3 \rightarrow O_3^* + O_2$$
$$Cl^* + O_3 \rightarrow O_3^* + Cl$$
$$Cl_3^* + O_3 \rightarrow O_3^* + Cl_2 + Cl$$

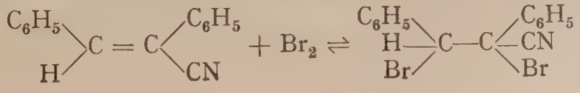
and $$O_3^* + O_3 \rightarrow 3O_2,$$

leads to a quantum yield of two and to zero order with respect to ozone, but the objections urged above (p. 556) to Cremer's mechanism apply equally here. It must be admitted that so far no satisfactory scheme for this reaction has been suggested.

We are equally in the dark in regard to the interpretation of the O_3—Br_2 reaction for which Bonhoeffer obtained a quantum yield of 30. Reaction chains of some type must intervene in this case, and the process requires further investigation to determine how the length of the chain varies with the experimental conditions. Unpublished work carried out by J. W. Belton and the authors shows that both chlorine and bromine catalyse the *thermal* decomposition of ozone, the latter being a particularly efficient catalyst, but the somewhat non-reproducible character of the results has up to the present prevented attempts to link up the thermal and photochemical reactions. It might, however, be mentioned that under certain conditions decomposition of ozone in mixtures with bromine occurs quite rapidly at room temperatures, but the fact that no after-effect occurs in the photochemical reaction suggests that the thermal and photochemical reactions have different mechanisms.

The active radiation for the chlorine-sensitised decomposition of ozone lies in the blue, violet, and near ultra-violet portions of the spectrum—radiation which is not appreciably absorbed by ozone. If, however, red light be employed, a direct (not a sensitised) reaction takes place, the radiation now being absorbed mainly by the ozone. This reaction was investigated by Bodenstein, Harteck, and Padelt (*Z. anorg. Chem.*, **147,** 233, 1925), who found that on insolating mixtures of chlorine and ozonised oxygen (strong in ozone) with red light, a liquid separated which on analysis was found to be the oxide Cl_2O_6. Considerable decomposition of ozone into oxygen occurs simultaneously. The same oxide is also formed on illumination of ClO_2 (Bowen, *J.C.S.*, **123,** 2328, 1923; Bowen and Booth, *ibid.*, **127,** 510, 1925). It is thus clear that the reactions in $Cl_2—O_2—O_3$ mixtures follow entirely different courses according as to whether red or blue light is employed, i.e. according as to whether O_3 or Cl_2 is the absorbing substance. In the latter case no oxide formation is observable (though naturally one cannot exclude the possibility of the formation and destruction of an unstable intermediate compound); in the former case we have the preliminary formation of activated ozone molecules, some of which decompose into oxygen while others oxidise chlorine, eventually to Cl_2O_6 but possibly through the intermediate formation of Cl_2O_3.

Sensitisation by Bromine.—We have already discussed one example of a bromine-sensitised reaction, the bromine-sensitised transformation of maleic ester into fumaric ester, a process which, like the bromine-sensitised decomposition of ozone, is associated with a high quantum yield. This process has been interpreted in terms of a mechanism involving bromine atoms and a radical (monobrominated maleic ester) whose average life period is high. Another bromine-sensitised reaction which probably proceeds *via* the intermediacy of bromine atoms is the reversal of the bromination of α-phenylcinnamonitrile, a process already briefly discussed in connection with photochemical equilibrium (p. 391). If a CCl_4 solution containing bromine and the nitrile be exposed to blue light, a photostationary state is eventually reached, due to the opposing reactions represented by



$$\begin{matrix} C_6H_5 \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} C_6H_5 \\ CN \end{matrix} + Br_2 \rightleftharpoons \begin{matrix} C_6H_5 \\ H \\ Br \end{matrix}\!\!>C—C<\!\!\begin{matrix} C_6H_5 \\ CN \\ Br \end{matrix}$$

According to Berthoud and Nicolet (*Helv. Chim. Acta*, **10**, 417, 1927), the reaction from right to left is a photosensitised process, occurring with appreciable speed only in the presence of bromine. The photostationary state is independent of the light intensity and is defined by the relation

$$\frac{\{[A] + m[ABr_2]\}[Br_2]}{[ABr_2]} = K,$$

in which [A] and $[ABr_2]$ are the concentrations of nitrile and dibromcompound respectively, and m is a constant whose value is 1·35. When nitrile is present in sufficient excess, the expression reduces to the mass action equation

$$\frac{[A][Br_2]}{[ABr_2]} = K.$$

The decomposition of the dibromide is an example of an autosensitised reaction. In a solution of the dibromide in CCl_4, the rate of decomposition is inappreciable at the commencement of insolation, but it is accelerated when the concentration of bromine becomes appreciable. The course of reaction thus follows the characteristic autocatalytic curve of Fig. 51.

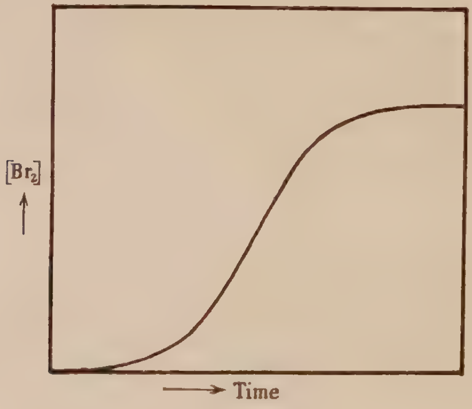


FIG. 51.

The observed rate of addition of Br_2 to the nitrile is the difference between the rates of the forward and reverse reactions. When the absorption of light is complete, this rate is given by

$$-\frac{d[Br_2]}{dt} = +\frac{d[ABr_2]}{dt} = k_a I_0^{\frac{1}{2}}[Br_2] - k_b I_0^{\frac{1}{2}} \frac{[ABr_2]}{[A]},$$

and for feeble absorption, by the relation

$$-\frac{d[Br_2]}{dt} = +\frac{d[ABr_2]}{dt} = k_a I_0^{\frac{1}{2}}[Br_2]^{\frac{3}{2}} - k_b I_0^{\frac{1}{2}}[Br_2]^{\frac{1}{2}} . \frac{[ABr_2]}{[A]}.$$

The rate of bromination (considered separately) is thus the same as that obtaining in the bromination of stilbene and cinnamic acid, in which cases the reverse reaction does not take place (cf. p. 454). It is clear that the quantum yield in either the direct or the reverse reaction depends on the experimental conditions; Berthoud, however, showed that chain mechanisms must be operative, as with blue light quantum yields of the order of 90 were obtained.

The mechanism of reaction suggested is the same as that advanced for the photo-brominations of cinnamic acid and stilbene, except that an extra reaction (6) must be added for the reverse process. Thus we have

(1) $Br_2 + h\nu \rightarrow 2Br$, (2) $A + Br \rightarrow ABr$, (3) $ABr + Br_2 \rightarrow ABr_2 + Br$,
(4) $2ABr \rightarrow A_2Br_2$, (5) $ABr \rightarrow A + Br$, (6) $ABr_2 + Br \rightarrow ABr + Br_2$.

These yield for the stationary state concentrations, when the absorption of light is weak,

$$[ABr] = \sqrt{\frac{2k_1 I_0[Br_2]}{k_4}}$$

and

$$[Br] = \frac{k_4[ABr] + k_3[Br_2] + k_5}{k_2[A] + k_6[ABr_2]} \cdot \sqrt{\frac{2k_1 I_0[Br_2]}{k_4}}.$$

The velocity of formation of dibromide (neglecting the reverse reaction) is thus given by

$$\frac{d[ABr_2]}{dt} = k_3[ABr][Br_2] = k_3\sqrt{\frac{2k_1}{k_4}} \cdot I_0^{\frac{1}{2}}[Br_2]^{\frac{3}{2}} \quad . \quad (1)$$

agreeing with that found empirically.

The velocity of decomposition of the dibromide (considered alone) is calculated to be

$$-\frac{d[ABr_2]}{dt} = k_6[ABr_2][Br]$$

$$= k_6 \cdot \frac{k_5 + k_4[ABr] + k_3[Br_2]}{k_2[A] + k_6[ABr_2]} \cdot \sqrt{\frac{2k_1}{k_4}} \cdot I_0^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}[ABr_2].$$

Now, since the quantum yield of the reaction is high (about 90), the velocity of reaction (4) which ends the chains must be small compared with that of reaction (3) and hence $k_3[Br_2] \gg k_4[ABr]$. Also, it is considered probable that $k_5 \gg k_3[Br_2]$, i.e. the radical ABr has a short life period. With this assumption the rate of decomposition of the dibromide becomes

$$-\frac{d[ABr_2]}{dt} = \frac{k_6 k_5}{k_2[A] + k_6[ABr_2]}\sqrt{\frac{2k_1}{k_4}}\, I_0^{\frac{1}{2}}[Br_2]^{\frac{1}{2}}[ABr_2] \quad . \quad (2)$$

which is not in disagreement with experiment. From equations (1) and (2) the equilibrium state is seen to be defined by the relation

$$k_3[Br_2] = \frac{k_6 k_5}{k_2[A] + k_6[ABr_2]} \cdot [ABr_2]$$

which may be written in the form

$$\frac{\left\{[A] + \frac{k_6}{k_2}[ABr_2]\right\} . [Br_2]}{[ABr_2]} = \frac{k_6 k_5}{k_3 k_2} = K.$$

This agrees with the expression found experimentally ; the term m in the latter is now seen to be the ratio $k_6 : k_2$.

The examples of bromine-sensitised processes hitherto discussed—ozone decomposition, transformation of maleic ester, and decomposition of the dibromide of α-phenylcinnamonitrile—are all reaction in which high yields of product per absorbed quantum are obtained. Not all cases of sensitisation by bromine show this behaviour, however, at least one well-authenticated case being known in which the quantum yield is normal and which presumably has a simpler mechanism. The reaction referred to is the oxidation of CCl_3Br by dissolved oxygen

$$O_2 + 2CCl_3Br \rightarrow 2COCl_2 + Cl_2 + Br_2,$$

investigated by Grüss (*Z. Elektrochem.*, **29,** 144, 1923). The rate of this reaction, which is another example of autosensitisation, depends only on the rate of absorption of light by the sensitising bromine. It shows the same independence on the concentration of reactants as does the chlorine-sensitised decomposition of ozone. The quantum yield (molecules of Br_2 formed per quantum absorbed) is practically unity; it is independent of the concentrations of O_2 and of CCl_3Br within wide limits—of CCl_3Br for example between the limits of pure CCl_3Br and a CCl_4 solution in which the ratio moles CCl_4/moles CCl_3Br is 15. It is not possible at present to interpret these results ; the simplest mechanisms involving primary dissociation of bromine into atoms appear to require quantum yields double that experimentally observed. If, on the other hand, activated Br_2 molecules be postulated which must collide with O_2 molecules, they must have a long average life—greater than $1{\cdot}5\ 10^{-7}$ sec.—as follows from the fact that the quantum yield is independent of $[O_2]$ down to a concentration of $2{\cdot}3 . 10^{-3}$ mole/litre.

Sensitisation by Iodine.—One example of an iodine-sensitised reaction will here be considered, the oxidation by dissolved oxygen of HI in aqueous solution

$$4HI + O_2 \rightarrow 2H_2O + 2I_2.$$

Lemoine (*Ann. Chim. Phys.*, [v], **12,** 240, 1877) found that this reaction takes place in the dark, but is accelerated by light, especially in the blue and violet. Other workers demonstrated that the photoreaction is markedly sensitive to catalytic influences ; thus Pinnow (*Ber.*, **34,** 2528, 1901) found that quinine and fluorescein and Gomberg (*Ber.*, **35,** 133, 1902) that ether, benzene, and chloroform are positive catalysts. The kinetics of the " light " and " dark " reactions have been investigated by Plotnikow (*Z. physikal. Chem.*, **58,** 214, 1907 ; **64,** 215, 1908), Winther (*Z. physikal. Chem.*, **108,** 236, 1924), and

Berthoud and Nicolet (*Helv. Chim. Acta*, **10,** 475, 1927), but with contradictory results.

Plotnikow, using solutions containing KI and HCl through which oxygen was bubbled, concluded that the rate of the dark reaction is given by

$$\frac{d[\mathrm{I_2}]}{dt} = k[\mathrm{HCl}]^{\frac{2}{3}}[\mathrm{KI}]^{\frac{2}{3}}[\mathrm{O_2}],$$

and that of the photo-reaction by a similar expression but with k replaced by $k'I_0$. These results differ markedly from those of Winther and of Berthoud, which, though not in accord in all essentials, do agree in certain respects. Winther finds that the dark reaction in solutions containing KI and HCl and traversed by a constant current of air or of oxygen has a velocity

$$\frac{dc}{dt} = k_1 + k_2 c,$$

in which c is the concentration of titratable iodine. The coefficients k_1 and k_2 are complex functions of the concentrations of reactants, and according to Winther are given by

$$k_1 = A[\mathrm{KI}]^2[\mathrm{HCl}][\mathrm{O_2}]^{\frac{3}{2}} \,.\, 10^{-B[\mathrm{KI}]^{\frac{1}{3}}}$$
$$k_2 = C[\mathrm{KI}]^4[\mathrm{HCl}]^{\frac{1}{2}}[\mathrm{O_2}]^{\frac{3}{4}} \,.\, 10^{-D[\mathrm{KI}]^{\frac{1}{3}}},$$

in which A, B, C, and D are constants. For the photo-reaction, the influence of the concentration of the sensitiser iodine was not studied by Winther, all his experiments being carried out with solutions initially containing sufficient iodine to absorb practically all the incident (monochromatic) light. The influence of O_2, KI, and HCl on the velocity of the photo-reaction, Winther expressed by the relation

$$\frac{dx}{dt} \propto [\mathrm{HCl}]^{\frac{1}{2}}[\mathrm{KI}]^4[\mathrm{O_2}]^{\frac{3}{4}} \,.\, 10^{-E[\mathrm{KI}]^{\frac{1}{3}}}.$$

A remarkable result was obtained for the effect of light intensity. Using monochromatic light of $\lambda = 366\,\mu\mu$, it was found that the velocity at first increases proportionately to the light intensity, then increases less rapidly than proportionality requires, afterwards goes through a maximum, and then decreases when I_0 is very large. Winther's theory of the reaction mechanism is somewhat elaborate. He assumes that in a given time interval a certain fraction of I_3' ions are in a state capable of absorbing light of a given frequency, but that only such ions as absorb one quantum become "photochemically activated," but not those absorbing two or more quanta. Further, the $\mathrm{I_3}'$ ions which are activated are supposed capable of emitting short wave light (ultra-violet) which is absorbed by I′ ions, the latter then reacting with oxygen. We will not discuss these assumptions or the further implications of Winther's mechanism, but instead pass on to a consideration of the work of Berthoud, whose results, differing somewhat from those of Winther, point to a simpler mechanism and one more in harmony with recent developments of the photochemistry of the halogens.

Berthoud and Nicolet employed solutions of KI and H_2SO_4 (not HCl). The velocity of the dark reaction was found to be given by

$$\frac{dc}{dt} = k_1 + k_2 c^{\frac{1}{2}},$$

in which, therefore, the process catalysed by iodine is semimolecular with respect to iodine, and not unimolecular as found by Winther. k_1 and k_2 are functions of the concentrations of reactants and are respectively

$$k_1 \propto [H_2SO_4][O_2]^m[KI]^{\frac{1}{2}}$$

and

$$k_2 \propto [H_2SO_4]^{\frac{1}{2}}[O_2][KI]^n,$$

in which $m > 1$, and $n < 1$ and decreases with increasing [KI].

For the photo-reaction, red light, which is feebly absorbed by the iodine, was used, and the observed rate of reaction under the experimental conditions employed was about ten times that of the dark reaction. The effect of the latter may be neglected for reasons analogous to those discussed in Chapter XII. (p. 668). The results obtained for the velocity of the photo-reaction are summarised by the expression

$$\frac{d[I_3']}{dt} = k_0 I_0^{\frac{1}{2}}[I_3']^{\frac{1}{2}}[H_2SO_4]^{\frac{1}{2}}[KI]^x[O_2],$$

in which x is an exponent which—greater than unity with small values of [KI]—decreases markedly with increasing concentration of [KI]. Also, the exponent of $[O_2]$ is not quite unity, but appears to be about 0·9. The chief difference between the results thus summarised and those found by Winther lies in the effect of light intensity, which according to Berthoud influences the reaction rate proportionally to $I_0^{\frac{1}{2}}$, a relation also obtaining for blue light. No indication that the rate of reaction goes through a maximum on increasing the intensity was obtained, even when the complete spectrum of a 4000 c.p. light was used.

The square root relation between velocity and energy absorbed naturally suggests a mechanism in which iodine atoms function. The heat of dissociation of iodine is 35,200 cal. per mole, which corresponds to a quantum of wave-length of about 800 $\mu\mu$. Hence, although with red light ($\lambda = 650$-$800\ \mu\mu$) which lies well on the long wave side of the convergence limit for $I_2(\lambda = 499\ \mu\mu)$ primary dissociation of I_2 is not possible, it is not unreasonable to postulate that the activated I_2 molecule resulting from light absorption dissociates on collision with other molecules. Berthoud advances the following reaction scheme as worthy of consideration :—

(1) $I_2 + h\nu \rightarrow 2I$
(2) $I + O_2 \rightarrow IO_2$
(3) $IO_2 + 4I' + 2H_2O \rightarrow 2I_2 + I + 4OH'$
(4) $IO_2 \rightarrow I + O_2$
(5) $2I \rightarrow I_2$
(6) $I_2 + I' \rightleftharpoons I_3'$,

which leads to

$$\frac{d[\mathrm{I_3'}]}{dt} = 2k_3[\mathrm{IO_2}][\mathrm{I'}]^n = 2k_3k_2\sqrt{\frac{2Kk_1}{k_5}} \cdot \frac{[\mathrm{I'}]^{n-\frac{1}{2}}}{k_4 + k_3[\mathrm{I'}]^n} \cdot I_0^{\frac{1}{2}}[\mathrm{I_3'}]^{\frac{1}{2}}[\mathrm{O_2}],$$

where n is the exponent for $[\mathrm{I'}]$ in the kinetic expression for the velocity of process (3). This mechanism accounts for the effects on the velocity of intensity of light, of the concentrations of the sensitising I_3' ions and of $[O_2]$, and also to some extent for the effect of I' ions, but fails to suggest an explanation of the influence of acidity (H_2SO_4). It is clear that this sensitised oxidation is a very complex process, whose mechanism, like those of all photo-reactions in which oxygen and the halogens interact, will doubtless remain obscure for some time, though Berthoud's work seems to take account of the main features of the reaction. It is to be observed that the reaction is one with a quantum yield greater than unity, though naturally γ will vary greatly with the experimental conditions. Winther obtained values of γ between 6·5 and 70 with monochromatic light of wave-lengths between 280 $\mu\mu$ and 436 $\mu\mu$, while Berthoud using blue light presumably of greater intensity found in one experiment $\gamma = 2{\cdot}7$.

Though of no particular photochemical significance, an example of what has been termed a pseudo-reversible reaction may now conveniently be considered. If a solution containing phosphorous acid and hydriodic acid and through which a steady current of air or oxygen is maintained be subjected to light, a pseudo-equilibrium state is set up under certain conditions. The " equilibrium " is due to the rate of formation of I_2 by

$$(1)\ 4\mathrm{HI} + \mathrm{O_2} \rightarrow 2\mathrm{I_2} + 2\mathrm{H_2O}$$

being balanced by its rate of disappearance by

$$(2)\ 2\mathrm{H_3PO_3} + 2\mathrm{H_2O} + 2\mathrm{I_2} \rightarrow 2\mathrm{H_3PO_4} + 4\mathrm{HI}.$$

The " equilibrium " reached is not a true photostationary state, however, since it depends for its maintenance on the net process (sum of (1) and (2))

$$(3)\ 2\mathrm{H_3PO_3} + \mathrm{O_2} \rightarrow 2\mathrm{H_3PO_4},$$

that is, on progressive consumption of phosphorous acid and of oxygen. With sufficient phosphorous acid present and a steady supply of O_2, it is found (Luther and Plotnikow, *Z. physikal. Chem.*, **61,** 524, 1907) that a stationary concentration of iodine is reached which is dependent on the light intensity. Reaction (3) takes place only as a catalysed process (i.e. *via* (1) and (2)) and reaction (2) is not light-sensitive. We therefore obtain

$$+\frac{d[\mathrm{I_2}]}{dt} = f(I_0) \,.\, F\{[\mathrm{HI}], [\mathrm{O_2}], [\mathrm{I_2}]\},$$

in which $f(I_0)$ and $F\{\ .\ .\ .\ \}$ are functions of the light intensity and of the concentrations of HI, O_2, and I_2; while

$$-\frac{d[I_2]}{dt} = k[H_3PO_3][I_2].$$

With H_3PO_3 and HI present in such excess that their concentrations may be considered constant and with constant supply of oxygen, it is seen that the pseudo-equilibrium concentration of I_2 is defined (for a light of given quality) by the light intensity, and that the same photostationary concentration of I_2 will be attained starting either with no I_2 present or with a concentration in excess of the photostationary one, a result confirmed by Luther and Plotnikow. Such cases as this of pseudo-reversible equilibria, which of course are dependent on an irreversible process, are not uncommon in both thermal and photochemical reactions. Examples are found in the oxidation of various organic substances by atmospheric oxygen in presence of such oxygen carriers as iron and uranyl salts (see below).

SENSITISATION BY FERRIC SALTS AND URANYL SALTS.

Characteristic photochemical reactions are those entered into by certain metallic salts, in particular by uranyl and iron salts. They consist essentially of the oxidation of organic substances (usually hydroxy-acids, alcohols, and dicarboxylic acids); at the same time Fe^{+++} or U^{++++++} ions are reduced to Fe^{++} or U^{++++} ions, or alternatively atmospheric oxygen is absorbed and the metallic salt acts as an oxygen carrier. Some of these reactions may be regarded as direct photo-reactions, for example, the reaction between uranyl sulphate and formic acid—

$$UO_2SO_4 + HCOOH + H_2SO_4 + \text{Light} \rightarrow U(SO_4)_2 + CO_2 + 2H_2O.$$

Others, such as the decomposition of oxalic acid in presence of a uranyl salt, are (mainly) photosensitised processes—

$$H_2C_2O_4 + (UO_2SO_4) + \text{Light} \rightarrow CO_2 + CO + H_2O + (UO_2SO_4).$$

There may, however, be some doubt as to the category of a given process, owing to the fact that it is not easy to specify with exactness the absorbing entities in certain systems; thus, the uranyl oxalate reaction might be regarded as a direct photo-reaction of the type

$$UO_2C_2O_4 + H_2SO_4 + \text{Light} \rightarrow UO_2SO_4 + CO + CO_2 + H_2O.$$

Certain authors have classed the action of iron and uranyl salts as examples of photocatalysis, but this name is better reserved for cases in which the catalyst does not absorb light of the wave-length employed. In the cases with which we shall deal, the activating light is absorbed by the metallic constituent, which in general may be regarded as the photosensitiser.

The function of these substances as oxygen carriers mentioned above may be illustrated by the case of ferric oxalate. On illumination (with visible light) in aqueous solution, this salt is reduced—

$$Fe_2(C_2O_4)_3 + h\nu \rightarrow 2FeC_2O_4 + 2CO_2.$$

The ferrous oxalate is, however, slowly oxidised by atmospheric oxygen—

$$2FeC_2O_4 + \tfrac{1}{2}O_2 + H_2C_2O_4 \rightarrow Fe_2(C_2O_4)_3,$$

and thus under appropriate conditions the net effect of illumination is simply the oxidation of oxalic acid—

$$H_2C_2O_4 + \tfrac{1}{2}O_2 \rightarrow 2CO_2 + H_2O.$$

Similar oxidation-reduction reactions take place in solutions containing uranyl salts and certain organic compounds when a current of oxygen is passed through the solution. The literature on these photochemical reactions has been summarised by Plotnikow (*Lehrbuch der Photochemie*); here we will deal only with a few of the best known examples.

The strong photosensitising action of iron salts is well exhibited in the so-called Eder reaction, which has been employed for actinometric purposes. The reaction is

$$2HgCl_2 + (NH_4)_2C_2O_4 \rightarrow Hg_2Cl_2 + 2NH_4Cl + 2CO_2.$$

The Eder solution is sensitive to visible light, but, as shown by Winther (*Z. wiss. Phot.*, Vols. **7** and **8**), only because the reactants normally contain traces of iron which acts as a photosensitiser. If carefully purified materials are employed, visible light is without action on Eder's solution, though ultra-violet light (of wave-length 300 $\mu\mu$) is effective. According to Winther, 0·047 milligram of $FeCl_3$ per litre suffices to produce detectable formation of calomel in blue light; this result points clearly to a high quantum yield for the process, though no measurements to confirm this have yet been carried out.

The reaction mechanism is undoubtedly a complicated one. Among other interesting observations, Winther has shown that the Eder reaction is retarded by addition of *excess* $FeCl_3$ and that this retardation is increased by diminution of the amount of dissolved oxygen. Also, a solution of $FeCl_3$ or $Fe_2(SO_4)_3$ which has been preserved in the dark causes no precipitation of calomel when added to Eder's solution. If, however, the solution of the ferric salt is pre-illuminated, immediate calomel formation ensues on mixing the two solutions. This suggests that reduction of ferric salts to ferrous salts takes place on insolation, the latter then reducing the mercuric chloride—

$$Fe^{+++} + \text{Light} \rightarrow Fe^{++}$$
$$Fe^{++} + Hg^{++} \rightarrow Fe^{+++} + Hg^{+}.$$

The reactions which occur in Eder's solution (containing iron) on illumination would then be

$$(1)\ 2FeCl_3 + h\nu + (NH_4)_2C_2O_4 \rightarrow 2FeCl_2 + 2NH_4Cl + 2CO_2$$
$$(2)\ 2FeCl_2 + 2HgCl_2 \rightarrow 2FeCl_3 + Hg_2Cl_2.$$

Reaction (2) is not, however, a spontaneous thermal process, but must be coupled in some way with process (1) or with the oxidation of ferrous oxalate by dissolved oxygen. If a solution of a ferrous salt and Eder's solution both free from oxygen are mixed, no precipitation of calomel occurs, but addition of oxygen induces the reaction. It is therefore probable that, while reactions (1) and (2), which as written do not form a chain mechanism, represent to some extent the reaction course, other intermediary reactions intervene. It might plausibly be suggested that in the latter some catalyst is formed and re-formed which has the effect of causing reactions (1) and (2) to recur many times per quantum absorbed.*

Winther (*Z. wiss. Phot.*, **8,** 135, 1910) has also investigated reaction (1), the photochemical interaction of ferric chloride and ammonium oxalate, and has discovered a type of solarisation, in some respects analogous to that of the photographic plate. For the latter it is found that the blackening action of light as given on the developed plate—the development being carried out in all cases in exactly the same way—first increases as the radiant energy is increased, goes through a maximum for a certain value of the incident energy E, and then decreases with still higher values of E. A similar phenomenon is encountered if aqueous solutions containing ferric chloride and ammonium oxalate are exposed to light (when reaction (1) occurs) and then " developed " in the dark with solutions of mercuric chloride containing oxygen. Plotting the weights of calomel precipitated against the times of exposure of system (1) to light (of constant intensity), the curve goes through a maximum. This " solarisation " is not, however, due to anomalous behaviour of the photochemical reaction (1); in this, the ferrous chloride concentration increases continuously with increasing illumination, as shown by the fact that if the insolated solution is " developed " with ammoniacal silver nitrate and the precipitated silver weighed, no solarisation is observed. The phenomenon thus depends essentially on the complex nature of reaction (2). Reaction (1) is, however, not a simple process either; its quantum sensitivity, determined by Winther and Oxholt-Howe (*Z. wiss. Phot.*, **14,** 196, 1914), is high, and the value of γ depends on the concentrations, time, and other factors. Values of γ between 3 and 100 were found in this reaction and in other analogous processes such as the photo-reactions between $FeCl_3$ and the ammonium salts of succinic, tartaric, citric, and acetic acids.

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* Winther has shown that under appropriate conditions addition of *ferrous* sulphate to Eder's solution precipitates, in the dark, much more calomel than the stoichiometrically equivalent amount.

The reaction $Fe^{++} + Hg^{++} \rightarrow Fe^{+++} + Hg^{+}$ (in absence of oxalate) is also sensitive to light, and this photochemical reaction has been studied by Winther (*Z. Elektrochem.*, **18**, 138, 1912). The reaction is accompanied by a gain in free energy, and, since ions are involved, the process may be cited as an example of the conversion of the absorbed radiation into electrical energy, i.e. we have here a type of photogalvanic accumulator. The spontaneous reverse process $Fe^{+++} + Hg^{+} \rightarrow Fe^{++} + Hg^{++}$ takes place comparatively slowly at room temperatures so that appreciable quantities of energy may be " stored " by means of this photochemical reaction.

Another example of the photosensitising action of iron salts is, according to Baur (*Helv. Chim. Acta.*, **8**, 403, 1925), afforded by the photosensitivity of potassium ferrocyanide in aqueous solution. On illumination of alkaline solutions of $K_4Fe(CN)_6$ in presence of oxygen, reactions occur which are approximately summarised by the equation

$$4K_4Fe(CN)_6 + O_2 + 8KOH + 2H_2O \rightarrow 4Fe(OH)_3 + 24KCN.$$

Baur found, however, that precipitation of ferric hydroxide occurs only if the solution (before illumination) is contaminated with potassium *ferri*cyanide, and that the process is photosensitised by this substance. The mechanism suggested is that on illumination the equilibrium

$$[Fe(CN)_6]^{---} \rightleftharpoons Fe^{+++} + 6(CN)^{-}$$

is displaced to the right, and that the ferric ions so formed react with ferrocyanide

$$Fe^{+++} + [Fe(CN)_6]^{----} \rightarrow Fe^{++} + [Fe(CN)_6]^{---},$$

this being followed by oxidation of ferrous ions by dissolved oxygen, etc.

Much work has been carried out with uranyl salts in respect both of their fluorescence in the solid state and in solution and also of their photochemical properties. The best investigated photo-reactions of the uranyl salts are the photolyses of uranyl formate and uranyl oxalate. Though neither is (in the main) a photosensitised process, they may conveniently be considered in this section. Dealing first with the oxalate reaction, most workers have used mixtures of uranyl salts (sulphate or nitrate) and oxalic acid, since with solutions of uranyl oxalate alone a precipitate soon forms, and conditions of investigation become less favourable. The decomposition of oxalic acid in presence of uranyl sulphate has been thoroughly studied by Büchi (*Z. physikal. Chem.*, **111**, 269, 1924), who also summarises previous literature on the subject. With violet light (400-470 $\mu\mu$) three processes occur, represented stoichiometrically by

$$(1)\ H_2C_2O_4 \rightarrow H_2O + CO + CO_2$$
$$(2)\ H_2C_2O_4 \rightarrow HCOOH + CO_2$$
$$(3)\ C_2O_4^{--} + U^{++++++} \rightarrow U^{++++} + 2CO_2.$$

Reaction (3) occurs, however, only to a small extent (about 1 per cent. of the total) unless the acidity of the solution is high (presence of H_2SO_4 or large amounts of oxalic acid), but even then this reaction is not of importance. The main reaction is (1), but process (2) must also be considered, as under the experimental conditions employed it takes place to an extent of between 30 and 40 per cent. of the total. The production of formic acid is made possible by the fact that in the presence of oxalate, uranyl formate decomposition is retarded. The yield of reaction (2) is considerably repressed, however, if the acidity of the solution is increased by addition of excess oxalic acid, HCl, or H_2SO_4. Under such conditions, formic acid formation may represent only a few per cent. of the total reaction. Apart from this complexity of the reaction course, the photolysis of oxalic acid in presence of uranyl oxalate is a simple reaction, which has been recommended for use for actinometric purposes. As long as the concentration of oxalic acid exceeds that of the uranyl salt, the velocity of photolysis (amount of oxalic acid disappearing in unit time) is independent of the oxalic acid content and of the time. When $[H_2C_2O_4] < [\text{uranyl salt}]$ the velocity is approximately proportional to $[H_2C_2O_4]$. Systems of uranyl sulphate, nitrate, or oxalate with oxalic acid give quantitatively the same results, and the velocity of photolysis is to a considerable extent independent of additions (O_2, HCl, H_2SO_4, formic acid). The temperature coefficient of the reaction is unity, and Einstein's Law is obeyed (one molecule of oxalic acid disappears per quantum absorbed) as long as the oxalic acid content is greater than that of the uranyl salt. Büchi considers that the absorbing constituent of the solution is a complex of uranyl oxalate with oxalic acid, i.e. that in mixtures of uranyl sulphate and oxalic acid, complexes of the type $[UO_2(C_2O_4)_2]^{--}$ are present, and that these complexes—the light absorbing constituents—are the reactants. The reaction is thus not regarded as a photosensitisation in which uranyl sulphate absorbs the light and transfers energy to oxalic acid on collision.*

The photolysis of uranyl formate has been investigated by Hatt (*Z. physikal. Chem.*, **92**, 513, 1918), who employed solutions containing uranyl sulphate, formic acid, and sulphuric acid. The course of the reaction is, according to Schiller (*Z. physikal. Chem.*, **80**, 641, 1912), represented by the equation

$$UO_2SO_4 + HCOOH + H_2SO_4 \rightarrow U(SO_4)_2 + CO_2 + 2H_2O.$$

In its initial stages, the reaction appears to conform nearly to the requirements of Einstein's Law, Hatt finding $\gamma = 0{\cdot}4$ and Büchi $\gamma = 0{\cdot}7$. It is, however, retarded partly by a "light-filter" action of the urano-salt formed, but mainly by an anti-catalytic effect of the same substance. The reaction is also retarded by KCl, NaI, $FeCl_3$, and vanadyl sulphate. These effects are ascribed by Hatt to oxidation-reduction processes of the following type. The assumption is made that the primary process in the action of light on uranyl salts is an electrolysis, thus—

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* The decomposition of lactic acid or sodium lactate in presence of uranyl sulphate appears also to be a relatively simple process with a quantum efficiency of unity (Müller, *Biochem. Z.*, **178**, 77, 1926).

$$5U^{++++++} + h\nu \rightarrow 3U^{++++++++} + 2U^{+++}.$$

In the presence of iron salts, however, the reverse change rapidly occurs by the reactions

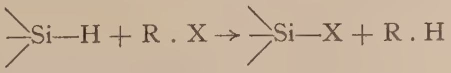
$$2U^{+++} + 6Fe^{+++} \rightarrow 2U^{++++++} + 6Fe^{++},$$

and $$3U^{++++++++} + 6Fe^{++} \rightarrow 3U^{++++++} + 6Fe^{+++},$$

and the $U^{++++++++}$ ions are not available for the oxidation of the formic acid.

SENSITISATION BY DYESTUFFS.

Uranyl salts which, as mentioned, are fluorescent both in the solid state and in solution, act as efficient sensitisers for the oxidation of organic acids and other similar processes. It is found that many dyes which fluoresce in solution are also good sensitisers of oxidation processes, and many investigators have sought to infer that a direct connection exists between capacity for fluorescence and power of photosensitisation. The best-known example of photosensitisation by dyes—though it does not fall within the purview of this work—is their action on the photographic plate, whereby the decomposition of AgBr in gelatine is made sensitive to red light which is absorbed by the dye. It has been suggested that the photosensitisation is due to the light re-emitted by the absorbing fluorescent dye (cyanine, erythrosine, etc.), but this view cannot be accepted, since the fluorescent emission of these substances lies in the blue region of the spectrum and is not produced by red light. One should rather infer that the connection between fluorescence and sensitisation is an indirect one; the sensitisers (uranyl salts and dyes) are particularly capable of absorbing light in a manner which does not lead to degradation of the absorbed energy into heat, but which preserves the energy as energy of activation for a short time, after which *either* re-emission as fluorescence *or* photosensitisation takes place. Photochemical theories of fluorescence have been discussed in a previous Chapter, as also have chemiluminescent reactions which lead to light emission by dyestuffs. However, in connection with their work on the chemiluminescence of silicon derivations, Kautsky and his collaborators* have made some interesting observations on photosensitisation which may here be mentioned. Siloxen (see Chapter VI.) reacts under suitable conditions with organic halides, substitution of a hydrogen atom in an Si—H group taking place according to



$$>\!Si{-}H + R.X \rightarrow\ >\!Si{-}X + R.H \quad . \quad . \quad (a)$$

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* Kautsky and Thiele, *Z. anorg. Chem.*, 144, 197, 1925.

in which R is an organic radical and X a halogen. If water is present in the system the halogen-siloxen formed is hydrolysed—

$$\equiv\mathrm{Si}-\mathrm{X} + \mathrm{H_2O} \rightarrow \equiv\mathrm{Si}-\mathrm{OH} + \mathrm{HX} \qquad . \qquad . \quad (b)$$

and oxysiloxens result. For these reactions to take place, preliminary activation of siloxen is necessary. This may be effected either by the agency of light, in which case we have a (sensitised) photochemical reaction, or as a consequence of the occurrence in the same medium of a suitable exothermic thermal reaction. The latter event affords an example of an "induced reaction." Considering the photochemical mode of activation, the reaction which occurs is due, not to absorption of light by the siloxen, but to traces of oxysiloxens always present in siloxen; these give rise to a greenish fluorescence and also sensitise the photochemical reaction (*a*). Since in the presence of water these oxy-bodies are themselves formed by process (*b*), the net reaction is an autocatalytic one and forms another example of autosensitisation. As the reaction proceeds, the system acquires sensitivity to red light, which initially it did not possess. At the start the small amount of oxy-compounds present do not appreciably absorb red light, and a mixture of siloxen, ethyl bromide, and water is insensitive to light which has been filtered through a solution of $K_2Cr_2O_7$, which removes rays of wave-lengths shorter than 550 $\mu\mu$. If, however, the reaction mixture be exposed for a short time to daylight, whereby higher oxidation products are formed, the system becomes sensitive to red light.

Sensitisation to red light may also be effected by addition of dyestuffs which absorb in that spectral region and which are adsorbed on the surface of the siloxen. Thus, rhodamine is active in this sense; it is necessary, however, that the dye be in intimate contact with the siloxen surface (by adsorption), which also goes to show that it is not a fluorescence of the dye which causes the photochemical reaction, but direct transfer of the energy absorbed by the dye to the adjacent molecules of siloxen. Kautsky thus considers that the fluorescence which may be emitted either by the oxysiloxens or by the dye stands in no causal relation to the photosensitised reactions initiated by these substances.

The only cases of sensitisation by dyes for which the quantum yields have been determined appear to be (*a*) the photosynthesis of carbohydrates in green leaves, and (*b*) certain oxidation processes in which again the sensitiser is chlorophyll. We shall not discuss here the photosynthetic process, whose energetics have been studied by O. Warburg and Negelein (*Z. physikal. Chem.*, **106,** 191, 1923) and by Wurmser (*Compt. rend.*, **181,** 374, 1925), but only deal with the results obtained by Gaffron (*Ber.*, **60,** 755, 1927) for the photo-oxidation of allylthiocarbamide in acetone solution in the presence of chlorophyll. On illumination, a solution of chlorophyll in acetone absorbs oxygen with gradual oxidation of the absorbing dyestuff. If, however, a suitable "acceptor" be present, the rate of absorption of oxygen is increased though the oxidation of the chlorophyll itself is retarded. The net effect under these conditions is then practically the photosensitised oxidation of the acceptor. The sensitiser used was "ethyl chlorophyllid" (Willstätter and Stoll, *Untersuchungen über Chlorophyll.* Berlin, Springer, 1913), and the acceptor was allylthiocarbamide, which is not sensibly oxidised in the dark either in presence or in absence of the dye. The photo-reaction was found to be a simple one, the oxygen absorption being proportional to the energy absorbed, and further, under certain conditions the quantum yield (molecules O_2 disappearing per quantum) was unity at the four wave-lengths 655, 578, 546, and 436 $\mu\mu$. The condition for unit quantum yield is that the ratio of acceptor concentration to chlorophyll concentration (C_A/C_F) be sufficiently great (for example, $C_A = 750 . 10^{-3}$ moles/litre and $C_F = 1{\cdot}54 . 10^{-3}$ moles/litre). The variation of γ with C_A/C_F is the same for all wave-lengths and is reproduced by the equation $\gamma = \frac{C_A . K}{C_A . K + C_F}$, in which K is a constant having the value 0·2. This equation shows that with constant dye concentration C_F, the value of γ increases with increasing concentration of acceptor C_A, reaching for large values of C_A the limiting value of unity. Further, the quantum yield depends only on the ratio C_A/C_F and not on the wave-length. This very simple behaviour cannot be accounted for on the assumption of the formation of a complex between dye and acceptor, as may easily be shown. Rather, dye and acceptor exist as such in solution, excess dye retards the reaction, excess acceptor promotes it, while the solvent is indifferent. Similar behaviour was also found with another fluorescent dyestuff—hæmatoporphyrin—and the same acceptor allylthiocarbamide. We have, therefore, in these cases the remarkable result that even under such conditions that the yield predicted by Einstein's Law is not attained, the value of γ for a given solution is independent of λ, or, otherwise expressed, a quantum of any size produces the same chemical effect in a given mixture. This is also the result found by Warburg and Negelein (*loc. cit.*) for the action of light on the living plant.

Other examples of photosensitisation by organic dyes are given by Weigert ("Die Chemischen Wirkungen des Lichts," *Ahrens Sammlung*, **17,** 183, 1912); in view, however, of the complex nature of the absorbing substance, little progress has been made in elucidating the nature of the photosensitisations to which they give rise, and brief mention of a few cases is all that seems to be required here. Most of the processes sensitised by dyes are oxidations by atmospheric oxygen; another much-studied reaction in this category is the Eder reaction. Gros (*Z. physikal. Chem.*, **37,** 157, 1901) found that photochemical oxidations of leuco-bases resulting in the formation of coloured substances are sensitised by dyes; since the reaction product is a sensitiser in many such cases, these processes form further examples of autosensitisation. The oxidation of HI in aqueous solution, which, as we have seen, is sensitised by iodine (I_3' ions), is also sensitised by fluorescing dyes such as quinine and acridine salts (Pinnow, *Ber.*, **34,** 2828, 1901). Of practical and biological significance is the "photodynamic action" of fluorescent dyestuffs on certain bacteria, toxins, etc., which are killed when illuminated under suitable conditions in presence of oxygen and the dye (Jodlbauer and Tappeiner, *Die sensibilisierende Wirkung fluoreszierender Substanzen*, Leipzig, 1907). The same investigators and also Gros (*loc. cit.*) found that Eder's reaction was strongly catalysed by dyes of the fluorescein series, and Winther (*Z. wiss. Phot.*, **9,** 205, 1911) has studied the reaction in more detail, using eosin as sensitiser.

The types of reaction hitherto studied are thus seen to be very similar to certain of those of iron, uranyl, and vanadyl salts. These oxidation reactions appear to be exo-energetic processes, most of which probably have high quantum yields and complex kinetics. There is one reaction, however, in which a coloured organic substance acts as a sensitiser to a process which is *endo-energetic*—the action of chlorophyll in photo-assimilation. Here, the net reaction is strongly endothermic, though it has been suggested by Noack (*Naturwiss.*, **18,** 383, 1926) that the first stage in photosynthesis is a photo-oxidation. He finds that chlorophyll may sensitise an oxidation reaction in aqueous solution—the oxidation of benzidine to benzidine blue—and also cites the strong "photo-dynamic action" of chlorophyll on bacteria as an oxidation process. Noack and also Tswett (*Z. physikal. Chem.*, **76,** 413, 1911) believe that the action of chlorophyll in photosynthesis is closely connected with its capacity for fluorescence, a view which has been criticised by Pringsheim (*Fluorescenz und Phosphorescenz*, Berlin, 1928). Other theories of the rôle played by chlorophyll in the photoassimilation process will be found in Spoehr's *Photosynthesis* (American Chemical Society Monographs).

MISCELLANEOUS EXAMPLES OF PHOTOSENSITISATION.

Before discussing theories of photosensitisation, one or two further examples will briefly be discussed. An interesting case of photosensitising action in a gaseous system is afforded by the photodecomposition of nitrogen pentoxide N_2O_5. This substance is insensitive to light of wave-lengths greater than 400 $\mu\mu$, but decomposes when mixed with nitrogen peroxide and exposed to blue light ($\lambda = 400$-$460\ \mu\mu$) (Daniels and Johnston, *J. Amer. Chem. Soc.*, **43,** 72, 1921). The *thermal* decomposition of N_2O_5—which, as the best authenticated example of a true unimolecular process, has been of great importance from a theoretical standpoint—is not, however, affected by N_2O_4 or NO_2. Fazel and Karrer (*J. Amer. Chem. Soc.*, **48,** 2837, 1926) have suggested that the mechanism of photosensitisation by NO_2 in this case is simply transfer, by collisions of the second kind, of energy from activated NO_2 molecules to pentoxide molecules which then decompose. Norrish (*Nature*, **119,** 123, 1927) advances an alternative explanation.

He has found (cf. p. 386) that on illumination of nitrogen peroxide, a photostationary state is set up which is represented by

$$(1)\ 2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2.\dagger$$

In the presence of N_2O_5, however, instead of the reversal of the photo-reaction, reaction

$$(2)\ N_2O_5 + NO \rightarrow 3NO_2$$

will take place. On this view, the decomposition of N_2O_5 would not be a " true " photosensitised process, but a thermal reaction between N_2O_5 and one of the products of the primary photo-process. Yet the net result of the whole reaction is, of course, simply the decomposition of N_2O_5 into nitrogen peroxide and oxygen, thus—

$$\begin{array}{c} 2N_2O_5 \rightarrow 4NO_2 + O_2 \\ \downarrow\uparrow \\ 2N_2O_4 \end{array}$$

This theory appears to be preferable to that of Fazel and Karrer. That reaction (2) takes place rapidly as a thermal reaction has been demonstrated by Busse and Daniels (*J. Amer. Chem. Soc.*, **49**, 1257, 1927), who also find that the photo-decomposition of N_2O_5 (sensitised by NO_2) is not affected by the presence of inert gases such as H_2, N_2, or O_2, a result to be anticipated on Norrish's theory, though it does not disprove the collision theory. Busse and Daniels further showed that bromine is not a photosensitiser for the decomposition of N_2O_5, though it absorbs strongly in the same region of the spectrum as does NO_2.

Sensitised reactions of a different type are the newly-discovered

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† The photo-reaction $2NO_2 \rightarrow 2NO + O_2$ has also been studied by Dickinson and Baxter (*J. Amer. Chem. Soc.*, **50**, 774, 1928), whose experiments were conducted under such conditions that the reverse change could be neglected. By employing sufficiently small partial pressures of NO_2, the rate of the trimolecular recombination of NO and O_2 was made very small, and determinations of the quantum yield of the photolysis of NO_2 could be made, the reaction being then practically irreversible. For the quantum yields, expressed as molecules of oxygen formed per quantum absorbed, the following values were obtained :—

$$\lambda = 435\ \mu\mu,\ \gamma = 0{\cdot}0046\ ;\ \lambda = 405\ \mu\mu,\ \gamma = 0{\cdot}36\ ;\ \lambda = 366\ \mu\mu,\ \gamma = 0{\cdot}77.$$

These values were not markedly dependent on the pressure of NO_2—N_2O_4 over the range studied (4–50 mm.). The absorption spectrum of NO_2 being discontinuous, the most probable reaction mechanism is the formation of an activated NO_2 molecule as a consequence of light absorption, followed by collision with a non-activated molecule. From the observed sharp increase in γ in passing from $\lambda = 435\ \mu\mu$ to $\lambda = 405\ \mu\mu$, one might infer either (1) that the probability that an NO_2^* molecule reacts instead of losing its excess energy by thermal degradation increases rapidly in this spectral region, or (2) that there is a critical energy level which an NO_2^* molecule must attain if reaction is to occur, that this energy level is somewhat higher than that corresponding to $\lambda = 435\ \mu\mu$, but that when light of this wave-length is employed the deficiency may be made up from the translatory energy of the colliding molecules.

ones in which the sensitiser is zinc oxide. Though these are processes in heterogeneous systems containing a solid sensitiser and hence lie outside the scope of this book, brief mention will here be made of them as they present certain features of interest. Eibner (*Chemiker Zeitung*, **35,** 753, 1911) found that Prussian blue is reduced in the light by zinc oxide in the presence of a depolariser such as glycerine or sugar. Raaschou (cf. Winther, *Z. wiss. Phot.*, **21,** 141, 1922) showed that dyes are decolorised on illumination in mixtures with ZnO and glycerine, and that under the same conditions white lead darkens owing to formation of colloidal lead. Winther (*loc. cit.*) investigated a variety of similar processes and concluded that zinc oxide acts as a photosensitiser (it remains unchanged as a result of the process), but that the action is conditioned by the presence of a trace of impurity in the oxide of zinc. In further experiments (*Z. wiss. Phot.*, **21,** 168, 1922) he showed that oxygen is transformed into ozone on illuminating zinc oxide in presence of air with light transmitted by glass ($\lambda > 340\ \mu\mu$). Baur and Perret (*J. Chim. phys.*, **23,** 97, 1926) investigated the photosensitising action of zinc oxide on certain processes in aqueous solution in contact with the solid. They found that silver nitrate is reduced according to the equation

$$2AgNO_3 + ZnO \rightarrow 2Ag + \tfrac{1}{2}O_2 + Zn(NO_3)_2.$$

An unstable peroxide of silver is possibly an intermediate reaction product. The disappearance of the zinc oxide in this case is due to a side reaction, and is not regarded as inherent in the photolysis itself. With a solution of $HgCl_2$ in contact with ZnO, illumination causes the reaction

$$2HgCl_2 + ZnO \rightarrow Hg_2Cl_2 + \tfrac{1}{2}O_2 + ZnCl_2$$

to take place, and again the disappearance of the sensitiser is regarded only as a secondary process. A third reaction studied by Baur and Perret was the photolysis of methylene blue in presence of zinc oxide, a reaction leading to simultaneous formation of an oxidation product and a leuco-derivative.

THEORIES OF PHOTOSENSITISATION.

The various theories which have been proposed to account for the phenomenon of photosensitisation have been discussed by Berthoud (*Trans. Faraday Soc.*, **21,** 554, 1926), who concludes that the different explanations which have been given may each be valid for particular cases. The theories which have been suggested include the following:—

(1) The view that photosensitisation is due to energy transfers by collisions of the second kind. This theory, deriving from the work of Franck and Cario on the sensitised decomposition of hydrogen and the sensitised fluorescence of Tl in presence of Hg, would certainly seem to be valid for mercury-sensitised reactions. Possibly there are other

cases which also fall into this category, though they do not appear to be many. Sensitisation by the halogens, which formerly might have been here included, must now be regarded—if the hypothesis of primary dissociation be accepted—as belonging to another group.

(2) The hypothesis that photosensitisation is caused by formation of a complex between the sensitiser and reactant, the complex being the absorbing substance which decomposes under the action of light, regenerating the sensitiser. This view has been suggested, for example, for the uranyl sulphate-oxalic acid reaction and for sensitisation of the photographic plate by dyes, but is not regarded favourably by Berthoud (*loc. cit.*), who cites some results obtained by Henri and Wurmser (*Compt. rend.*, **156,** 230, 1913) on light-absorption by acetaldehyde as telling against this hypothesis. Henri and Wurmser infer that the chemical action of light on an organic compound is limited to the atomic grouping to which the absorption is due (aldehyde group, acid group, etc.). In spite of this it does not seem to us that the "complex" theory is *a priori* an improbable one; naturally, in a complex molecule, the further apart the absorbing and the acceptor groups are, the more difficult must such transfers of energy become, but in certain molecules or molecular complexes, favourable conditions for the postulated energy interchange might be present. The cases envisaged by this theory gradually merge into those classified under theory (1). In dilute gaseous systems we have examples of energy transfers by collisions of the second kind, in more concentrated systems these might insensibly change into reciprocal actions between absorbing and neighbouring molecules "during the act of absorption," and finally in other cases we might have reciprocal actions of the electronic systems of absorbing and acceptor molecules before the act of light absorption, with formation of loose or possibly definite complex compounds, which then become the "true" absorbing constituents of the system.

(3) The theory that sensitisers are fluorescent substances, whose emission provokes the photochemical reaction. This view has been discussed above, with the conclusion that, in general, it is not applicable. A modification of it is the theory of Winther (*Z. wiss. Phot.*, **21,** 175, 1922), who believes that "an optical sensitiser is a selectively absorbing substance, which possesses—in a spectral region different from that at which sensitisation occurs—the same absorption as the acceptor (i.e. the system whose reactivity is enhanced), or which on illumination forms a second system which, on returning to its original form, emits radiation which can be absorbed by the acceptor. The condition for strong sensitisation is that the sensitiser is either present in a different phase to that of the acceptor (example: sensitisation by ZnO) or is present in such small concentrations that it cannot itself absorb an appreciable part of the secondary radiation (example: ferrous oxalate)." The secondary radiation in the cases cited is supposed to be of very short wave-length (less than 200 $\mu\mu$), and the frequently observed retardation of photochemical reactions by oxygen to be due

to the strong absorption of this radiation by oxygen. The theory originated from Winther's experiments on the formation of ozone on illumination of zinc oxide in presence of oxygen, a reaction which ordinarily requires short wave radiation. Though no alternative explanation of Winther's results has been suggested, his theory does not appear to be well founded. The emission of such short wave radiation contradicts Stokes' Law, which, in spite of the appearance in many cases of anti-Stokes terms in the photoluminescence, is in general agreement with experiment, and also direct physical tests for the postulated emission by ZnO have so far yielded negative results.

(4) The hypothesis that the primary action of light is to form a substance which (acting as a catalyst) enters into reaction with an acceptor, initiating a sequence of reactions which regenerates either the sensitiser or the catalyst. This mode of action is considered by Berthoud to be the most frequent method of photosensitisation. Examples are found in the reaction mechanisms proposed by Berthoud for the bromine-sensitised decomposition of the dibromide of phenylcinnamonitrile and the iodine-sensitised oxidation of HI in solution, in both of which processes primary formation of halogen atoms is postulated, followed by a series of changes which regenerate these catalysts. Another and simpler example is the mechanism advanced by Winther for the sensitisation of the Eder reaction by ferric salts. Here, absorption of light is presumed to activate ferric ions, which then react with oxalate and are themselves reduced to ferrous ions. The latter are then re-oxidised by mercuric chloride.

This mode of sensitisation must doubtless be effective in many cases, and, at least for the halogen-sensitised reactions which have high quantum yields, the assumption of primary formation of halogen atoms followed by " chains " regenerating these atoms forms on the whole a satisfactory picture of the nature of photosensitisation in such processes, though naturally the specific hypotheses regarding the nature of the intermediate products of short life period (radicals, etc.) may require further justification.

Baur (*Helv. Chim. Acta*, **1,** 186, 1918) has advanced a theory of the nature of molecular activation by light, which—as it has been applied mainly to photosensitised reactions—may here be discussed. It may be regarded as a modification of the theory under discussion, or possibly of the hypothesis of energy transfer from the sensitiser to reactant by collision. Baur considers that the elementary process in the action of light is the formation of a polarised molecule. If photochemical reaction subsequently ensues, this is regarded as a type of " electrolysis," in which the " anodic " and " cathodic " constituents of the polar activated molecule react with depolarisers present in the system. Applied for example to uranyl salts, illumination is supposed to cause the formation of states of higher and lower oxidation, thus—

$$5U^{VI} + \text{Light} \rightarrow \begin{cases} 3U^{VIII} \\ 2U^{III} \end{cases},$$

or more generally

$$U^{VI} + \text{Light} \rightarrow U^{VI}\left\{\begin{array}{l}\oplus\\ \ominus\end{array}\right.$$

in which $U^{VI}\left\{\begin{array}{l}\oplus\\ \ominus\end{array}\right.$ represents the polarised molecule. The system thus formed has both oxidising and reducing properties; its action on oxalic acid is represented by Baur as

$$U^{VI} + \text{Light} \rightarrow U^{VI}\left\{\begin{array}{l}\oplus + C_2O_4^{--} \rightarrow CO_2\\ \ominus + C_2O_4^{--} + 2H^+ \rightarrow CO + CO_2 + H_2O\end{array}\right\} + U^{VI}.$$

For the oxidation of HI by O_2 in presence of quinine, the reaction is represented as

$$\text{Quinine}\left\{\begin{array}{l}\oplus + I^- \rightarrow \tfrac{1}{2}I_2\\ \ominus + \tfrac{1}{4}O_2 + H^+ \rightarrow \tfrac{1}{2}H_2O\end{array}\right\} + \text{Quinine},$$

and for the decomposition of $AgNO_3$ sensitised by ZnO, by

$$ZnO\left\{\begin{array}{l}\oplus + OH^- + Ag^+ \rightarrow \text{Peroxide} + \tfrac{1}{2}H_2O\\ \ominus + Ag^+ \rightarrow Ag\end{array}\right\} + ZnO.$$

Whilst this theory of an analogy between electrochemistry and photochemistry is doubtless of interest, its applications are limited, and indeed the method adopted for expressing the chemical change, in which apparently simultaneous collisions of the anodic and cathodic depolarisers with the activated molecule are necessary, can hardly be regarded as corresponding to actuality.

Summing up, we may say that most cases of photosensitisation appear, in the present state of our knowledge, to be best interpreted on the basis of theories (1) and (4). Theory (2) possibly holds in some cases, but it is unlikely that theory (3)—the hypothesis of fluorescent emission—is valid. The above considerations hold for reactions in liquid and gaseous systems; for solid systems, especially for the photographic plate, other factors such as adsorption must be taken into account in discussing the nature of optical sensitisation, chemical sensitisation, and desensitisation.

CHAPTER XII.

PHOTOCHEMICAL CATALYSIS AND INHIBITION. TEMPERATURE COEFFICIENTS. AFTER-EFFECTS.

PHOTOCHEMICAL CATALYSIS AND INHIBITION.

THE velocity of all photochemical reactions may be increased or diminished by the addition of substances which are not themselves consumed in the process under consideration. The influence of such substances may be of diverse kinds, and it would be difficult to enumerate all the types of phenomena which may arise, and any classification at the present state of our knowledge would be an arbitrary one. Roughly, however, we must distinguish between cases in which the added substance absorbs the activating light and others. In the former event, if the addition hastens the reaction, we have examples of photosensitisation; on the other hand, if the reaction is retarded, this is due to "internal filter action," possibly accompanied by a "negative photocatalytic effect". The term photocatalyst is best applied to substances which increase the speed of the photo-process without themselves absorbing radiant energy; similarly, inhibitors (or negative photocatalysts) are non-absorbing substances which retard a photochemical reaction, though, as mentioned, true inhibition may be present when the added substance absorbs the effective light. Probably the most striking examples of photocatalytic action are those exerted by traces of water vapour, and marked inhibition of many photochemical reactions is effected by oxygen in small amounts. Finally, as is the case with thermal reactions in liquid media, the nature of the solvent in photochemical reactions often exerts a marked influence on the velocity. These form the main types of "catalytic" action which will here be discussed.

According to modern views of the nature of photochemical reactions, the effect of foreign substances may be of two kinds; they may influence the primary light process or they may modify the velocities or alter the course of the succeeding secondary processes. The second of these influences would, in general, appear to be the more frequent, though there are but few cases in which the mechanism of photocatalytic action has been satisfactorily established. The first effect—modification of the primary process—may or may not be associated with a change in the extinction of the absorbing substance, or, better expressed, theories of photocatalytic action in certain cases postulate a change in the efficiency of the primary process unaccompanied by detectable alteration in the absorption. Thus, water vapour profoundly modifies the velocity of the hydrogen-chlorine reaction, and this effect is regarded by certain investigators as being due to a change in the nature of the primary process. Again, according to Allmand and Webb (*Z. physikal. Chem.*, **131,** 189, 1928), sodium chloride increases the quantum yield of the photolysis of sodium hypochlorite in aqueous solution, an increase which they interpret as a neutral salt effect on the primary photolytic process, regarded as $OCl' + h\nu \rightarrow Cl' + O$. They also point out that various electrolytes including NaCl increase the quantum efficiency of the photo-decomposition of potassium ferrioxalate in solution, and also of solutions of potassium cobaltioxalate (Jaeger and Berger, *Rec. trav. chim.*, **40,** 156, 1921). Possibly in these reactions, in which the photolysis of an ion occurs, the salt effect is of the same nature. On the other hand, Allmand, Cunliffe, and Maddison (*J.C.S.*, p. 655, 1927) interpret the results of their work on the photolysis of chlorine water in the sense that strong electrolytes in general lower the efficiency of the primary photo-reaction resulting from quantum absorption. Other reactions retarded by chlorides and particularly by hydrochloric acid are the photochemical reduction of $TiCl_4$ in presence of alcohol (Benrath and Obladen, *Z. wiss. Phot.*, **22,** 47, 65, 1922), the photolysis of uranyl acetate (Baur and Rebmann, *Helv. Chim. Acta*, **5,** 221, 1922), and the interaction of $FeCl_3$ and oxalic acid (Lemoine, *Ann. Chim.*, **6,** 433, 1895).

The term photocatalysis has been applied by different writers to a variety of phenomena. One legitimate application is that which deems photocatalytic reactions those in which the action of light hastens the attainment of the ordinary equilibrium state at the given temperature and pressure—in other words, all exo-energetic processes accelerated by light. We shall, however, use the term in the narrower sense above defined, viz. photocatalysis is the acceleration of a photochemical reaction already taking place by the addition of a substance which does not itself absorb the radiation used. This definition might be regarded as too narrow, since it appears to exclude the effect of water vapour on the hydrogen-chlorine reaction in visible light; if however, we make the assumption that even in absence of water this reaction still takes place, but with immeasurably slow velocity, our definition may—legitimately perhaps—be retained. With regard to the possibility of such catalysis in any given reaction, little may be said except that there is a rough distinction between exo-energetic and endo-energetic processes. In the former, the quantum yield may have any (positive) value, which could conceivably be increased by addition of a suitable substance. For reactions which are endo-energetic, however, especially for those markedly so, the prospects for the appearance of positive catalytic action are not so favourable, though undoubtedly they exist. In these processes the bulk of the energy necessary for reaction to occur must be supplied by the absorbed radiation and the yield (and rate) of reaction is limited. Though one must be careful not to postulate that the upper limit to the yield is that which may be calculated from the ratio of the heat of reaction to the energy absorbed, a certain yield—most probably of this order of magnitude—must in all cases be the maximum attainable. In endo-energetic reactions in which the yield is already high and approximating to this limit, no added substance is likely to exert a positive catalytic effect. On the other hand, the possibility exists of finding positive catalysts for other endo-energetic processes in which the yield is considerably smaller than the limit. We should thus expect as a rule to encounter photocatalytic action chiefly in exo-energetic processes and in slightly endo-energetic processes. For reactions which are very light-sensitive, positive catalytic effects are in general not to be anticipated, since the rates of such reactions depend largely on the lengths of the "chains," which are already very great and which are more susceptible to inhibiting effects of added substances than to positive effects. Yet, according to Padoa (*Gazzetta*, **51,** 193, 1921), the hydrogen-chlorine reaction is positively catalysed by traces of iodine whose action is regarded not as a photosensitisation (though naturally it absorbs some of the activating light) but as essentially photocatalytic.

It cannot be said that in many cases do we know the mechanism of positive catalytic action. It is likely, however, that in many reactions the effect of the catalyst is not primarily concerned with the photochemical part of the reaction, i.e. with the primary process, but rather with the succeeding secondary reactions. In such cases, therefore, the mechanism of catalysis will be essentially similar to that obtaining in thermal processes. In the latter, and confining our attention to homogeneous systems, catalytic action would appear to be due in the main to one of two causes. Either the catalytic action involves association or compound formation between the catalyst and the reactants, with more rapid formation of the resultants than in the absence of the catalyst, or the action of the catalytic agent is due to its capacity to annul the action of inhibitors present in the system. From this point of view, therefore, catalysis in certain photochemical reactions is due to intermediate compound formation by the catalyst with the reactants of one of the secondary thermal processes concerned in the change. Possibly the influence of $H^{\cdot}$ ions on many photochemical reactions is of this type. In other cases, destruction by the catalyst of inhibitors may be suspected, as for example in the stabilising influence of iodine on the photo-bromination of toluene, an effect which is probably due to the annulment by iodine of the inhibiting action of oxygen. Another example of somewhat similar kind is the apparent positive effect of inert gases such as helium, argon, and nitrogen on the rate of photo-decomposition of ozone in visible light. Here, however, the influence of the inert gases is really a retarding effect, but since in each case the negative effect of the added gas is less than that of oxygen, comparison of the velocities of deozonisation (at the same total pressure) in ozonised oxygen and in ozonised oxygen in which part of the oxygen has been displaced by the inert gas appears to indicate a positive effect of the latter. In the presence of hydrogen, however, a true catalytic action is found, an action which is probably bound up with the formation of activated water molecules resulting from a side reaction, and which—by transfer of energy on collision—activate fresh ozone molecules.

Again, some cases of catalytic action may doubtless be due to a shift in an equilibrium caused by the catalyst whereby the concentration or "activity" of one of the reactants is increased. But no useful purpose is served by continuing the attempt to give examples of different types of catalytic action, since further data are needed before generalisations may be made. At the present state of our knowledge it is better to treat each reaction separately and to recognise that, even in seemingly simple cases, several factors may be operative in producing a net positive catalytic effect. We shall therefore only deal with one example of photocatalysis in detail—that effected by water vapour—though here again, in spite of much work, the mode of action is by no means settled.

Catalysis by Water Vapour.—In Chapter X. we have discussed at some length the catalytic effect of water vapour on the photochemical combination of hydrogen and chlorine; we now consider—though more briefly—other examples of photochemical gas reactions on which the influence of desiccation has been tested. Systematic experiments in this direction have been conducted by Coehn and Tramm (*Ber.*, **54,** [B], 1148, 1921; *ibid.*, **56,** [B], 455, 458, 1923; cf. especially Tramm, *Z. physikal. Chem.*, **105,** 356, 1923); the last of these papers contains also literature references to previous work on the influence of moisture on both thermal and photochemical reactions. Tramm employed for the purification and drying of the gases the method of fractional distillation at low temperatures, and in most of his experiments he avoided the use of chemical drying agents such as P_2O_5. The water vapour content of the gas mixtures was claimed to be less than 0·004 mm., and was probably considerably smaller. The reactions studied included

(1) the photochemical conversion of oxygen into ozone in ultra-violet light;
(2) the photo-combination of H_2 and Cl_2 in visible light, and the photo-decomposition of HCl in ultra-violet light;
(3) the photo-decomposition of HI and of HBr in ultra-violet light;
(4) the combination of CO and Cl_2 and of SO_2 and Cl_2 in visible light;
(5) the combination of H_2 and O_2 in ultra-violet light; and
(6) the photo-equilibrium $2CO_2 \rightleftharpoons 2CO + O_2$ in ultra-violet light.

The velocity of the ozonisation of oxygen in ultra-violet light was found to be unaffected by desiccation, the same velocity being obtained with $p_{H_2O} = 0{\cdot}004$ mm. and $p_{H_2O} = 10$ mm. The hydrogen-chlorine reaction has already been dealt with ; the reverse process—the photo-decomposition of hydrochloric acid, a reaction which proceeds with moist gas to a small extent *—was entirely prevented by drying. This result is of special interest since the rates of photo-decomposition of the other two halogen acids (HBr and HI) are, according to Tramm, independent of whether the gases are dry or moist. The quantum yield in these two gas reactions is thus 2 under all conditions hitherto tested ; on the other hand, the quantum yield of the decomposition of HCl is a function of the water content of the insolated gas.

The influence of drying on the reverse processes, the combination of H_2 and Br_2 (in the light and in the dark) and of H_2 and I_2 (in the dark), has been tested by Lewis and Rideal (*J. Amer. Chem. Soc.*, **48,** 2553, 1926). They claim that under both thermal and photochemical conditions the union of H_2 and Br_2 at temperatures up to 275° is completely inhibited in the absence of water, while even at higher temperatures reaction is much retarded. Further, they find that the thermal equilibrium point of the reaction $2HI \rightleftharpoons H_2 + I_2$ at 432°—which ordinarily lies at about 17·5 per cent. decomposition of HI—is shifted over completely to the right by intensive drying, a result which they interpret to mean that recombination of H_2 and I_2 is not possible in absence of water. The results for both reactions have, however, been criticised by Bodenstein and Jost (*J. Amer. Chem. Soc.*, **49,** 1416, 1927), who regard the retardations claimed by Lewis and Rideal as non-proven, and believe that reaction between the halogen acids and P_2O_5, present as drying agent in these experiments, was the cause of the observed effects.

An influence of moisture on the photochemical union of CO and Cl_2 in visible light has long been known, a retardation by drying having been observed by Wildermann (*Z. physikal. Chem.*, **42,** 257, 1903) and others. This result was confirmed by Tramm (*loc. cit.*), but the reaction was not completely inhibited by the degree of desiccation employed. On the other hand, Tramm showed that drying to the same extent prevented completely the photochemical union of SO_2 and Cl_2 in visible light, a reaction which Le Blanc (*Z. Elektrochem.*, **25,** 229, 1919) had previously found to be sensitive to moisture. It is thus seen that the velocities of at least three gaseous photochemical reactions of chlorine—with H_2, with CO, and with SO_2—are all functions of the partial pressure of water vapour present. Each of these processes has a high quantum yield and is thus a " chain " reaction.

Contradictory results have been obtained in respect of the influence of drying on the photochemical union of H_2 and O_2 in ultra-violet light. According to Tramm, drying has no effect on the velocity of combination. He used P_2O_5 as the drying agent in this case, and the degree of desiccation of the mixed gases was such that no explosion took place on heating to redness, but only slow combination. Baker (*J.C.S.*, **81,** 400, 1902) had, however, previously prepared a drier mixture, as shown by the fact that a silver wire could be melted in it without measurable action between the hydrogen and oxygen, and it was therefore possible that electrolytic gas more highly dried than that of Tramm would exhibit a different reactivity in ultra-violet light. The point has been tested by Baker and Carlton (*J.C.S.*, **127,** 1990, 1925), who did not confirm Tramm's conclusion. They found the velocity of photo-combination in damp gas mixtures to be much greater than that in the dried gases, and indeed in a few experiments with the latter no interaction whatsoever was obtained. Water must thus be regarded as a positive catalyst for this reaction, and Tramm's result must be ascribed either to insufficient drying or to a trace of impurity in the electrolytic gas used.

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* The photostationary state attained under the conditions of this work of Tramm's corresponded to 0·4 per cent. decomposition.

The opposing reactions $2CO_2 \rightleftharpoons 2CO + O_2$ in ultra-violet light have been studied by Chapman, Chadwick, and Ramsbottom (*J.C.S.*, **91,** 942, 1907), Coehn and Sieper (*Z. physikal. Chem.*, **91,** 397, 1916), and Coehn and Tramm (*loc. cit.*). Coehn and Sieper found that with dry gas the same photostationary state was attained from either side—a photo-equilibrium corresponding to 18 per cent. decomposition of CO_2 with the light used and with the system at atmospheric pressure. On the other hand, with damp gas the decomposition of CO_2 in the same apparatus was inappreciable (less than 0·3 per cent.). This shift in the photo-equilibrium is due, as shown by Chapman and his associates and by Coehn and Tramm, not to an acceleration of the photo-reaction $2CO + O_2 \rightarrow 2CO_2$ by water vapour, but to a *retardation* by moisture of the opposing photo-decomposition $2CO_2 \rightarrow 2CO + O_2$. The latter investigators found that a mixture of CO and O_2, so dry as not to react on sparking, reacted in ultra-violet light at the same speed as a damp mixture. Tramm (*loc. cit.*) showed that SO_2 also has a retarding effect similar to that of water vapour on the photo-decomposition of CO_2, dry carbonic acid gas containing small amounts of sulphur dioxide showing no detectable decomposition on exposure for 2 to 3 hours to ultra-violet radiation, while in absence of SO_2 but under otherwise identical conditions, 5 to 10 per cent. decomposition was observed. While one might infer from this result that the mechanisms of the action of H_2O and of SO_2 on this photo-process are similar, one should perhaps also draw the conclusion from the fact that SO_2 does not accelerate the *thermal combination* of CO and O_2 while water does (Dixon, *Trans. Roy. Soc.*, **175,** 617, 1884; *J.C.S.*, **49,** 94, 384, 1886), that the nature of the action of water on closely allied reactions might be very different from case to case.

These constitute the chief reactions for which careful investigation of the influence of traces of water vapour has been made. Though the results are of exceeding interest and importance for the general theory of photochemical (and thermal) processes, not much progress has yet been made towards elucidating the mechanism of catalysis by water, and little more can usefully be added at present. The discussion (in Chapter X.) of the rôle of water in the hydrogen-chlorine reaction indicates the types of theories which have been suggested for that process, and doubtless the same hypotheses (suitably modified where necessary) could be applied to other reactions catalysed by water. One of the most interesting of these cases is the negative catalysis of the photochemical decomposition of CO_2 by water vapour and by SO_2. Both retarding agents have high dipole moments, and it is probable, though not established, that their influence on the photo-reaction is a "physical" one. Franck (cf. Tramm, *loc. cit.*) has suggested that the light-activated CO_2 molecule forms a complex (a "quasi-molecule") with a non-activated CO_2 molecule. The metastable system

$$(CO_2{}^* \;..\; CO_2)$$

thus formed may then decompose as a result of a favourable collision according to

$$(CO_2{}^* \;..\; CO_2) \rightarrow 2CO + O_2.$$

If, however, collision with H_2O or SO_2 occurs, the complex loses its excess energy and reverts to CO_2—

$$(CO_2{}^* \;..\; CO_2) + H_2O \rightarrow 2CO_2 + H_2O + \text{Energy}.$$

Of the other cases studied, the effect of water on the photo-decomposition of HCl and the difference between this and the absence of effect on the photolysis of the other two halogen acids are of interest. The primary process in the latter reactions has been proved to be decomposition into hydrogen and halogen atoms "in one elementary act," and probably the same is true for HCl. If this is the case, one would anticipate that this primary process would be independent of water vapour, and hence that it is the secondary processes which are affected by drying. Yet in this, as in other cases, no definite conclusions may yet be drawn. Finally, attention may be directed to the influence of water vapour on the CO—Cl_2 reaction, an effect mentioned but not discussed in Chapter X., and consisting, together with positive catalysis, of a change in the reaction kinetics. In particular, a reaction rate proportional to the square root of the light intensity is changed by drying into a slower rate which is now proportional to the first power of the intensity. As we have seen, proportionality between the velocity of a photochemical reaction and the square root of light intensity may be accounted for if we assume that (*a*) light forms an active agent, the rate of whose formation is proportional to the light intensity, (*b*) the rate of destruction of this substance is proportional to the square of its concentration, and (*c*) the rate of the *net* (measured) reaction is proportional to the concentration of the active agent. The cases hitherto encountered of such photo-processes have been reactions of the halogens, and for each the assumption has been made that the active agent is a halogen atom (Cl, Br, or I); thus for the CO—Cl_2 reaction, Bodenstein supposes that the carriers of the chains are Cl_3 and Cl and also that the chains are broken by recombination of chlorine atoms—$Cl + Cl \rightarrow Cl_2$—a reaction whose velocity is proportional to $[Cl]^2$. Accepting this, one explanation of the influence of drying on the relation between light intensity and velocity of photo-formation of phosgene *might* be that in the dry gas the velocity of the reaction $Cl + Cl \rightarrow Cl_2$ is no longer proportional to $[Cl]^2$ but becomes proportional to [Cl]. This could come about, for example, if in the damp gas combination of chlorine atoms occurs in the gaseous phase, but on desiccation only on the walls of the containing vessel. In the latter case, the rate of combination would be proportional to the rate of diffusion of Cl atoms to the walls and hence proportional to [Cl]. Similar views have been advanced —though somewhat tentatively—by Kistiakowsky (*J. Amer. Chem. Soc.*, **49,** 2194, 1927) in connection with the difference in the Budde effects in wet and dry chlorine. Yet it cannot be said that the hypothesis carries us very far, since it is difficult to see how it is to account for the fact that drying *diminishes* the rate of photo-combination of CO and Cl_2. Rather, the reverse effect would be anticipated, since, on desiccation, the life of the Cl atoms would be increased with consequent increase in the stationary state concentration of Cl and in the rate of the net photochemical reaction. The suggestion above made, even if acceptable on other grounds, does not provide an explanation of the rôle of water in this photochemical reaction.

INHIBITION OF PHOTOCHEMICAL REACTIONS.

The phenomenon of " negative catalysis " or, as it is better called, inhibition has long been recognised and studied in both thermal and photochemical reactions. While in very few cases has agreement been reached in regard to the detailed mechanism of inhibitory action, there are some grounds for the belief that in many such reactions the broad outlines of satisfactory theories of " negative catalysis " are now being developed. Dealing very briefly with the inhibition of thermal homogeneous processes, these have been classified by Rideal and Taylor (*Catalysis in Theory and Practice*, p. 144, Macmillans, London) under the following heads :—

(*a*) Reactions inhibited by reduction of the concentration of a positive catalyst.
(*b*) Reactions inhibited by reduction of the concentration of a reacting constituent.
(*c*) Reactions inhibited by the shortening of a " chain " of reactions.

While it is recognised that this classification is possibly not exhaustive and also that our present knowledge does not suffice to make possible in each case a definite choice of one or other of these modes of action, the proposed scheme is a useful one, and it may be extended to photochemical reactions, the same limitations being admitted. For the latter class of reactions, we must also recognise at least one further possibility, namely, a " physical " action of the inhibitor on the primary process of absorption, or deactivation of light-activated molecules by collision with inhibitor molecules, resulting in either case in diminished capacity for chemical reaction.

In previous Chapters examples of inhibitory action have been cited, and in one case—the inhibition of the hydrogen-chlorine reaction by oxygen—theories of the mechanism of the inhibition have been discussed. It appears probable, though it is by no means established, that inhibition in this and in other photo-chlorinations (such as the $CO—Cl_2$ reaction and the chlorinations of benzene, toluene, and acetic acid) may be ascribed to breaking of reaction chains by oxygen (mechanism (*c*)). Other examples of inhibition most probably associated with the same mechanism are inhibitory effects observed in certain oxidations by oxygen gas, such as the oxidation of benzaldehyde and of Na_2SO_3, which, both thermally and photochemically, appear to be chain reactions. These are discussed below. An example of type (*b*), in which the inhibition may be ascribed to a reduction of the concentration of a reacting constituent, is the photo-reaction between hydrogen and bromine, which is retarded by HBr and thus exhibits "auto-inhibition." The action of the inhibitor in this case is, as we have seen (p. 464), to be ascribed to reduction in the concentration of atomic hydrogen by the reaction

$$H + HBr \rightarrow H_2 + Br,$$

with consequent diminution in the speed of the photo-reaction. Other examples of the same type of mechanism are, as pointed out by Rideal and Taylor (*loc. cit.*), to be expected when the actual reactant is an electrolytic ion (the undissociated molecule being inactive) and substances are added which repress the ionisation ; alternatively, if the undissociated molecule is the reactant, inhibition would be anticipated on addition of substances which increase the degree of dissociation. From this point of view, nearly all photo-processes taking place in aqueous solution should be sensitive to addition of electrolytes, and this is generally what is found. The inhibiting (or accelerating) effect is, however, usually small and not comparable to that obtaining in inhibition by mechanism (*c*). A third example of inhibition of type (*b*) (presumably) is that effected by KI on the photo-reaction between iodine and potassium oxalate ; the explanation given is that the reactant is the iodine molecule (and not the I_3' ion), and that addition of KI causes a shift in the equilibrium $KI + I_2 \rightleftharpoons KI_3$ in the direction unfavourable for the photo-reaction. With regard to cases of inhibition which may be ascribed to mechanism (*a*)—reduction of the concentration of a positive catalyst—these are not so well established for photochemical processes, and difficulty might be experienced in differentiating them from those of types (*b*) and (*c*). Examples are possibly to be found in certain photochemical reactions associated with after-effects, such, for example, as the conversion of *N*-chloroacetanilide into *p*-chloroacetanilide. This process taking place in solution in ethyl alcohol or glacial acetic acid is retarded by water, whose action would appear to be the destruction of catalysts formed in the course of the photo-reaction.

Retardation of photochemical reactions by deactivating collisions between excited and inhibiting molecules has been assumed to occur in many cases and would indeed be expected to be operative—at least to some extent—in all processes in which the primary action of light is to produce an activated molecule. Examples have been given in previous Chapters ; we might here recall, however, that the magnitude of the inhibition (i.e. of the presumed deactivation) depends in most, though not in all cases, markedly on the nature of both excited and deactivating molecules.

It is not claimed that the above-mentioned types of inhibition exhaust the possibilities, and indeed there have been advanced several theories of inhibition which could hardly be assigned to any of our groupings. Such, for example, are Winther's theory of inhibition (by oxygen) in terms of which the inhibitor reduces the active secondary radiation of high frequency (cf. p. 623), and Norrish's theory of inhibition of the H_2—Cl_2 reaction by NH_3 which postulates an action located on a glass surface (cf. p. 518). These are theories of a specialised nature and the claims for acceptance of neither are very strong. They do, however, both emphasise possibilities of inhibition of the essentially photochemical part of the net reaction, a standpoint which has been somewhat overlooked in our scheme, which was based on a classification of thermal reactions. Modes of inhibition other than those given and which do not obtain in thermal reactions will thus probably have to be recognised. Finally, attention may be drawn to the phenomenon of internal filter action (negative photosensitisation) which is of practical importance though of little theoretical significance. This is the retardation caused by the presence of a substance (an addition or a reaction product) which absorbs some of the effective radiation. In this case the observed diminution in reaction velocity is entirely accounted for by the diminution in the energy absorbed by the reactant (or sensitising) molecules. In such cases, which are not infrequent, it is necessary when measurements of quantum yields are being made to test whether the coefficient of absorption of the light-sensitive constituent is affected by the presence of the other absorbing substance, and also to apportion correctly the total energy absorption between the two substances. In what follows, discussion of inhibition will be limited to a few more or less typical cases, commencing with inhibition by oxygen.

Inhibition of Photochemical Reactions by Oxygen.—Oxygen acts as a powerful inhibitor to many photochemical processes. The H_2—Cl_2 and the CO—Cl_2 cases have already been dealt with. Luther and Goldberg (*Z. physikal. Chem.*, **56,** 43, 1906) showed that many other photo-chlorinations are also retarded by oxygen, the reactions investigated including the chlorination of benzene, of toluene, of xylene, and of acetic acid. On the other hand, they found that the bromination of benzene was not affected by oxygen. According to Luther and Goldberg, oxygen disappears by reaction in the course of these photo-chlorinations, so that the inhibition tends to decrease with time ; this is not always the case, for, as we have seen in the hydrogen-chlorine reaction, there is practically no diminution in the concentration of the inhibiting oxygen (when this is small) as the reaction progresses. Not only chlorinations but other types of reaction have been shown to be inhibited by oxygen ; amongst these are the photo-decomposition of ozone, the photo-bromination of toluene (Bruner and Czarnecki, *Bull. Acad. Sci. Cracow*, p. 516, 1910), the decomposition of ferric salts of organic acids in aqueous solution (Winther, *Z. wiss. Phot.*, **14,** 196, 1914), and the Eder reaction (Winther, *Z. wiss. Phot.*, Vols. **7** and **8,** 1909-1910). The effect of oxygen in the last of these photo-processes was also demonstrated by Jodlbauer and Tappeiner (*Ber.*, **38,** 2602, 1905), who showed that the sensitiveness of the Eder solution to light could be increased by passing hydrogen through it or by evacuation, whereas addition of oxygen was accompanied by a strong retardation. Winther (*loc. cit.*) investigated the nature of oxygen inhibition in this reaction ($2HgCl_2 + (NH_4)_2C_2O_4 \rightarrow Hg_2Cl_2 + 2NH_4Cl + 2CO_2$) which, as previously shown, takes place with visible light only in the presence of iron salts. The velocity of calomel formation thus depends not only on the illumination and on the concentrations of the reactants, but also on the concentrations of iron salt and of oxygen. With constant oxygen content and increasing concentration of ferric salt, the velocity at first increases, passes through a maximum, and becomes very small (if not nil) at high concentrations of iron salt. In the presence of small amounts of iron (when the sensitivity is high), addition of oxygen retards the reaction ; on the other hand with high concentrations of iron, oxygen increases somewhat the rate of the photo-reaction. Conditions are thus somewhat complex, and the complete resolution of the various part-processes has not been effected. The two chief reactions which occur are

$$(1)\ 2FeCl_3 + h\nu + (NH_4)_2C_2O_4 \rightarrow 2FeCl_2 + 2NH_4Cl + 2CO_2$$
$$(2)\ 2FeCl_2 + 2HgCl_2 \rightarrow 2FeCl_3 + Hg_2Cl_2.$$

The formation of ferrous salt by (1) is retarded by oxygen, owing to the fact that the ferrous salt is rapidly oxidised with consumption of the inhibitor ; this inhibition is the cause of the induction periods observed in the Eder reaction when oxygen is present in solution. The induction period is then the time required for the concentration of oxygen to decrease from its initial high value to some very small value. Process (2) is, however, not a simple thermal reaction (cf. p. 614) but is a highly complex process, coupled in some way with (1) and also dependent on the occurrence of a simultaneous oxidation of ferrous ions. Thus, it has been shown that if small amounts of a ferrous salt are added to Eder's solution in the dark, much more calomel may be precipitated than corresponds to ferrous salt added ; also, that if oxygen be *completely* excluded, no precipitation of calomel occurs. In the presence of small quantities of iron the velocity of formation of calomel as well as the amount of calomel precipitated per mole of ferrous salt is found to be the greater, the less oxygen there is present in solution ; connected with this is the retardation of the Eder reaction by oxygen when the concentration of iron is small. A similar connection persists in presence of large amounts of iron, when oxygen accelerates the Eder reaction and also promotes calomel formation when a ferrous salt is added to the Eder solution. The nature of reaction (2) and of the processes coupled with it is, however, obscure ; it is probable that the net reaction is one which is induced by the oxidation by dissolved oxygen of ferrous ions, and that activated molecules formed thereby initiate " chain " reactions which yield calomel and CO_2 as resultants. In the papers of Winther will be found additional details regarding the Eder reaction—a process which, in view of the complexities mentioned, is entirely unsuited for actinometric usage.

It has been mentioned above that the formation of a ferrous salt on illumination of a solution containing $FeCl_3$ and $(NH_4)_2C_2O_4$ (i.e. reduction of ferric oxalate to ferrous oxalate) is inhibited by oxygen. Jodlbauer (*Z. physikal. Chem.*, **59**, 513, 1907) showed, however, that the concomitant liberation of CO_2 is unaffected by oxygen ; the photochemical reaction considered alone is therefore not inhibited, but oxygen combines rapidly with the ferrous oxalate formed and hence causes an apparent induction period if it is the ferrous ion which is being measured. On the other hand, on insolation of ferric tartrate solutions, the amount of CO_2 liberated is greater in the presence than in the absence of oxygen. Here, of course, there is consumption of oxygen during exposure to light, the oxygen absorbed oxidising a portion of the tartaric acid anion to CO_2.

Another example of retardation by oxygen, and one which is in one respect similar to that of the Eder reaction, is found in the oxidation of quinine in aqueous solution by dissolved oxygen, a reaction studied by Weigert (*Nernst Festschrift*, p. 464, 1912). The rate of absorption of oxygen by irradiated quinine sulphate solutions was measured, and it was found that with constant concentration of quinine sulphate (0·1 per cent.), the rate of absorption of oxygen from a mixture of O_2 and N_2 containing 0·6 per cent. O_2 was thirty times greater than that from pure oxygen. Similar behaviour was obtained for the oxidations of fluorescein and erythrosin. In these processes, therefore, the non-absorbing reactant is itself an inhibitor, and this behaviour is in a way analogous to that found in the Eder reaction, where oxygen, though not a reactant, appears to be necessary for the change to occur, yet acts as an inhibitor. The nature of the inhibition has not been satisfactorily accounted for ; Weigert demonstrated, however, that the process (in the case of quinine) is a complex one and consists of at least two well-defined stages : (*a*) the absorption of oxygen by the quinine to form some compound or compounds which have the power of easily oxidising KI, and (*b*) the transformation of these into the final (unknown) products of reaction. He also suggested that his theory of the formation of a " heterogeneous catalyst "—a theory previously advanced in another connection—might be applicable here. According to this, the primary process would be the formation of the "heterogeneous catalyst," which, however, in this case must also be destroyed by oxygen. The process measured would take place after adsorption of quinine and oxygen on the reaction nuclei of the catalyst, whose stationary concentration (and hence the reaction velocity) would be the greater the lower the concentration of oxygen. There is, however, no evidence in support of the theory and contrary to the view that the reaction is homogeneous.

Weigert also showed that in the course of the reaction some of the oxygen was converted into a peroxide, in this case hydrogen peroxide, a substance also formed in the photo-oxidation of other substances such as amyl alcohol and oxalic acid. Peroxide formation is of interest as it is of technical significance in the production of rapid drying oils. It is believed that preliminary illumination of the oil causes the formation of a catalyst, a peroxide, which accelerates the autoxidation of the oil when it is exposed to atmospheric oxygen. Further reference is made to autoxidation processes and their connection with inhibition on p. 641. Finally, we may mention that the oxidation of quinine is inhibited by acid and is completely suppressed in the presence of $0{\cdot}1N$ HCl. (It is to be noted, however, that increase in the acidity of solutions containing quinine promotes the fluorescence, so that we have another example illustrating the inverse relation between fluorescence and photochemical action.) Weigert supposes that it is the quinine ion which is the light-sensitive constituent of the system, the diminished ionisation of the quinine salt in presence of the SO_4'' or Cl' ions of the added H_2SO_4 or HCl being thus the cause of the influence of these acids on the velocity of oxidation.

The mechanism of inhibition by oxygen has been the subject of much speculation, and attempts at theories of general applicability have been made by Bodenstein and by Winther among others. Bodenstein (*Z. physikal. Chem.*, **85**, 329, 1913) suggested, in connection with his classification of photochemical reactions into "primary" and "secondary" light reactions, that the latter type (in general, those possessing high quantum yields) are processes in which electrons are liberated, that these electrons enter into reactions which yield the resultants and regenerate electrons, and that oxygen inhibition is a general accompaniment of such reactions owing to the strong affinity possessed by oxygen for electrons. The theory has been negatived, however, by the fact that, though ionisation may be detected by delicate methods as an accompaniment to certain photochemical (and thermal) reactions, its extent is too small to render any other assumption necessary than that it is quite a secondary phenomenon, playing no essential part in the process. Also, not all of Bodenstein's "secondary" light processes are retarded by oxygen, as shown, for example, by the work of Boll and Henri (*Compt. rend.*, **158**, 32, 1914). Winther's theory (*Z. wiss. Phot.*, **21**, 175, 1922) has been previously discussed (p. 623); it postulates that secondary radiation in the short wave ultra-violet region of the spectrum is emitted by the absorbing substance, that this radiation is absorbed by the reactants, and that the inhibiting effect of oxygen is due to its strong absorption of this ultra-violet light. Modern views on the nature of inhibition by oxygen fall in the main into one of two categories: (*a*) deactivation of light-activated molecules on collision with oxygen, and (*b*) the breaking by oxygen of a chain, which, in general, is regarded as an "atom" or "radical" chain. Inhibition of the feebler type such, for example, as is encountered in the photo-decomposition of ozone by visible or ultra-violet light falls into group (*a*), while for marked inhibition such as that observed in the hydrogen-chlorine reaction, a possible explanation is that oxygen affects the "chain" of secondary thermal reactions, but not the primary process. Most of the theoretical and experimental work on inhibition by oxygen has been concerned with the reactions of the halogens, and it is of interest to note the cases of gaseous halogen reactions (both photochemical and thermal) on which the effect of oxygen has been tested. The hydrogen-chlorine reaction is retarded by oxygen both in the light and in the dark (Sachtleben, *Diss.*, Hannover, 1914), while the hydrogen-bromine reaction (thermal or photochemical) is unaffected. Also the $CO—Cl_2$ reaction is retarded by O_2 under certain conditions in the light, while neither the thermal combination of CO and Cl_2 nor the reverse decomposition of $COCl_2$ is inhibited by oxygen. These observations, together with that of the change in the photo-combination of CO and Cl_2 on increasing the temperature from a process inhibited by oxygen to one not so retarded, form important material for a survey of the phenomenon of inhibition, though their significance is not at present clear. One comment may, however, be made in respect of the marked difference in inhibitive effects of oxygen on the $H_2—Cl_2$ and $H_2—Br_2$ reactions. This is to point out that the difference may only be a consequence of the fact that the $H_2—Cl_2$ reaction is a "chain" process, the $H_2—Br_2$ reaction not. The latter is almost certainly an "atom" reaction involving H atoms; if we assume that the same is true for the $H_2—Cl_2$ reaction (let us postulate, for example, the Nernst mechanism), then in both reactions the inhibiting process $H + O_2 \rightarrow HO_2$ could occur. Now suppose that the same (small) percentage of oxygen be present in a hydrogen-chlorine and in a hydrogen-bromine mixture and that the relative probabilities of the reactions $H + O_2 \rightarrow HO_2$ and $H + Cl_2 \rightarrow HCl + Cl$ (or $H + Br_2 \rightarrow HBr + Br$) are in the ratio 1 : 20. Then it will be seen that while the addition of this quantity of oxygen should retard the $H_2—Br_2$ reaction by only 5 per cent. (a barely detectable amount), the hydrogen-chlorine reaction should be enormously retarded, the quantum yield falling from (say) 100,000 to 20, since the average number of links in the chain is simply the odds against a chain being broken (i.e. 20 to 1).

Inhibition of the Photo-decomposition of H_2O_2 and of Autoxidation Processes.—Further examples of inhibition most probably due to the breaking of thermal reaction "chains" are to be found associated with the photo-decomposition of H_2O_2 in aqueous solution and with certain photochemical (and thermal) oxidation processes. As we have seen, the photochemical decomposition of hydrogen peroxide in ultra-violet light is a complex process in which quantum yields between 10 and 100 are obtainable. The reaction is very susceptible to inhibition by a variety of substances, as shown by Henri and Wurmser (*Compt. rend.*, **157,** 284, 1913) and by Mathews and Curtis (*J. Physical Chem.*, **18,** 521, 1914). The phenomenon was later subjected to systematic investigation by Anderson and Taylor (*J. Amer. Chem. Soc.*, **45,** 650, 1210, 1923), who studied the inhibitory effects on this reaction of a number of inorganic and organic compounds. They found that with many classes of organic substances there was a marked connection between inhibitory power and absorption capacity, compounds strongly absorbing in the ultra-violet exerting the most powerful inhibitory effects. Such, for example, was the case with esters, acids, amides, and alkaloids. The inhibition is not, however, simply an " internal filter " action, due to the light absorbed by the inhibitor not being available for decomposing H_2O_2. This is shown by the fact that the inhibiting action is very considerably greater when the added substance is present in the H_2O_2 solution than when it is employed simply as an external light filter. Anderson and Taylor therefore suggest that the inhibition, while partly due to internal filter action, is, in the main, caused by the capacity of the inhibitor to break the " chains " of the H_2O_2 reaction,* this power being the greater the stronger the absorption of the inhibitor in the ultra-violet. The rule, however, is not generally applicable, since in a few cases—in particular with amines—strong inhibition was found with the added substance quite diactinic in the ultra-violet.

Recent work by F. O. Rice (*J. Amer. Chem. Soc.*, **48,** 2099, 1926) points to an explanation of inhibition of this reaction different from that given above. He finds that the presence of dust particles is the governing factor in the ordinary photochemical decomposition of H_2O_2, and that elimination of dust is accompanied by very marked diminution in the velocity of reaction. He suggests that substances which change the rate of decomposition (photocatalysts and inhibitors) function by promoting or poisoning the catalytic activity of the dust, that photocatalysts possibly act by causing increased adsorption of H_2O_2 on the dust, and that inhibitors displace H_2O_2 on the substrate by being themselves preferentially adsorbed. On the basis of these views, he denies the existence of reaction " chains " in this photolysis, but supposes instead that the whole aggregate of H_2O_2 molecules adsorbed on a dust particle decomposes when one quantum of ultra-violet light is absorbed by the cluster.

The " chain " theory of negative catalysis proposed by Christiansen (*J. Physical Chem.*, **28,** 145, 1924) has been applied by Bäckström

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* A chain mechanism for the reaction has been suggested by Kornfeld (see p. 460).

(*J. Amer. Chem. Soc.*, **49,** 1460, 1927; *Medd. K. Vetenskapsakad. Nobel-Inst.*, **6,** Nos. 15 and 16, 1927) and by Taylor (*J. Physical Chem.*, **32,** 516, 1928) to certain processes of oxidation by oxygen gas, the so-called autoxidation reactions. Christiansen suggested that homogeneous thermal reactions which are retarded by minute quantities of foreign substances might be chain reactions of essentially the same nature as photochemical chain reactions, and that negative catalysts are substances which have the power of breaking the reaction chains by abstracting excess energy from the " hot " molecules of intermediate products or by reacting with them. He further suggested that typical reactions of this type are autoxidation reactions, which have been the object of much attention—recently from Moureu and Dufraisse (cf. *Chem. Reviews*, Vol. III., No. 2, 1926). These investigators found, for example, that extremely small amounts of hydroquinone markedly retarded the autoxidation of acrolein, similar results being obtained with other oxidisable substances such as benzaldehyde, acetaldehyde, turpentine, linseed oil, etc. Bäckström (*loc. cit.*) supports Christiansen's view that these thermal reactions are " chain " processes. He found that certain of them are sensitive to light, that the quantum sensitivities of the " light " reactions are very large, that the photo-processes as well as the thermal reactions are susceptible to the action of inhibitors, and that there is parallelism between the two as regards the action of different inhibitors. The reactions studied were the oxidations of benzaldehyde, enanthaldehyde, and sodium sulphite (in aqueous solution). Using monochromatic light in the ultra-violet, each of these was found to be a " chain " reaction, the maximum quantum yields obtained being of the order 10,000, 15,000, and 50,000 respectively.* The inhibitors employed included diphenylamine, anthracene, and phenol for the benzaldehyde reaction, α- and β-naphthol and picric acid for enanthaldehyde oxidation, and various alcohols for the oxidation of sodium sulphite. It was found that an inhibitor for the light reaction invariably inhibits the dark reaction; in the case of the oxidation of benzaldehyde the dark reaction is the more sensitive to the action of inhibitors, while for the other two oxidation processes there is good parallelism between the action of inhibitors on the light and the dark reactions. In terms of the chain theory it would seem, therefore, that the activity of an inhibitor in breaking the chains is generally independent of whether the preliminary activation be thermal or photochemical.

In the interpretation of these autoxidation processes, some form of the intermediate compound theory of Bach, Engler and Wild, and others † is usually adopted. There is reason to believe that the type of process with which we are concerned takes place *via* the intermediate formation of a peroxide, thus:—

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* In calculating these quantum yields (molecules O_2 absorbed per quantum absorbed) the average " dark " rate was first subtracted from the rate observed on illumination. In many cases the " dark " rate was a considerable fraction of the total.

† For literature references see Rideal and Taylor, *Catalysis in Theory and Practice*, Macmillan, 1926.

$$(1)\ A + O_2 \rightarrow AO_2$$
$$(2)\ AO_2 + A \rightarrow 2AO.$$

In the oxidation of benzaldehyde, the intermediate compound (benzoperacid or benzoyl hydrogen peroxide, $C_6H_5 . CO . O . OH$) has been isolated. Bäckström found that with benzaldehyde both reactions (1) and (2) are sensitive to light, but that, while the quantum sensitivity of (1) may be of the order of 10^4, that of reaction (2) is much smaller (though the reaction itself is still a "chain"), yields of about 17 molecules per quantum being obtained. From this result the conclusion was reached that the reaction between benzaldehyde and oxygen is considerably more efficient in causing the activation of fresh aldehyde molecules than the one between aldehyde and peracid. It was further found that the three oxidations (of benzaldehyde, enanthaldehyde, and sodium sulphite) could be photosensitised and by the presence of suitable agents made sensitive to visible light (for example, benzil added to benzaldehyde makes the photo-oxidation sensitive to light of 436 $\mu\mu$). It appeared probable, however, at least in the case of the two aldehydes, that the mechanism of photosensitisation cannot simply be transference of energy from the excited sensitiser molecule to aldehyde, but that the sensitiser is itself oxidised and that the greater energy of activation of the resulting products initiates oxidation of the aldehyde.

The above three reactions and other autoxidations are characterised by high energy of reaction, and many of them exhibit the phenomenon of chemiluminescence (the oxidation of phosphorous is a noteworthy example). The work of Bäckström makes it likely that both the thermal and photochemical reactions are "chains" with the same mechanism of chain propagation. The exact nature of inhibition found in these reactions is, however, doubtful—it may be that the inhibitors are themselves consumed by oxidation in the course of the reaction, or that the energy they receive is dissipated as kinetic energy. There would appear to be some grounds for the view that at least in some cases the first hypothesis is correct, since many inhibitors are easily oxidisable substances. According to Taylor (*loc. cit.*), in the Na_2SO_3 reaction with alcohols as inhibitors, the inhibitor undergoes oxidation, and there is a definite relationship between the amounts of sulphite and of inhibitor which are oxidised. While the sulphite oxidised is found to be inversely proportional to the concentration of inhibitor, the inhibitor oxidised is constant over a wide range of concentration, even with different inhibitors whose efficiencies differ markedly. (These inhibitions would thus seem to be somewhat analogous to the effect of oxygen on the hydrogen-chlorine reaction, in which the quantum yield of water formation, i.e. of destruction of the inhibitor, is 2 and independent of the concentration of oxygen). Finally, it might be mentioned that the difference between the inhibitions of the dark and light reactions in the case of benzaldehyde oxidation and the concordance between the two for the sodium sulphite reaction are possibly connected with the relative rates of the part-processes (1) $A + O_2 \rightarrow AO_2$, (2) $AO_2 + A \rightarrow 2AO$ in the two cases. In the benzaldehyde reaction process (2) is relatively slow, but in the sulphite reaction it is fast, and according to Bäckström (*Medd. K. Vetenskapsakad. Nobel-Inst.*, **6,** No. 16, 1927) this difference suffices to account for the observed results.

While on the whole the " chain " theory gives a fairly satisfactory interpretation of these autoxidation reactions, there remain certain difficulties, to which brief reference may be made. The thermal oxidation of sodium sulphite is strongly catalysed by copper salts (Titoff, *Z. physikal. Chem.*, **45,** 641, 1903), but these are without influence on the photochemical rate. F. O. Rice (*J. Amer. Chem. Soc.*, **48,** 2099, 1926) finds that the thermal reaction, even in the presence of copper salts, is entirely a " dust " reaction, an optically clear solution of sodium sulphite absorbing no oxygen over a period of several hours. He therefore regards the reaction as heterogeneous, the catalytic activity of the dust particles being promoted by adsorption of copper and poisoned by a further coating of alcohols such as mannitol. We are thus faced with the same difficulties in interpreting this reaction as encountered in the case of the decomposition of H_2O_2, and it would seem that in both cases heterogeneous catalysis plays some part which is not taken into account by the " chain " theory. Again, for the photo-oxidation of sodium sulphite, in which quantum yields up to 5.10^4 are encountered, it is somewhat difficult to accept the view that the chains are activated molecule chains. This is seen when one recalls that the reaction takes place in aqueous solution (containing many more molecules of H_2O than of Na_2SO_3) in which there would seem to be ample opportunities for deactivation of " hot " Na_2SO_3 molecules by water molecules. For this reason, a chain mechanism involving radicals or atoms is preferable, and indeed, according to Franck (cf. Bäckström, *loc. cit.*), the type of absorption spectrum possessed by Na_2SO_3 might be an indication that absorption of ultra-violet light is accompanied by some type of dissociation of the molecule. Finally, these photo-oxidations are sometimes associated with after-effects, i.e. the " dark " rate following a period of insolation is greater than the preceding dark rate, and occasionally the velocity of the " after-effect " is greater than the photo-rate by which it was caused. Under these conditions, it is difficult to study the " light " reaction, and this, together with the erratic nature of the phenomena connected with thermal autoxidations, makes caution necessary in attempting to interpret such results as are obtained.

INFLUENCE OF SOLVENT MEDIUM ON PHOTOCHEMICAL REACTION VELOCITY.

The velocities of both thermal and photochemical reactions are in general highly dependent on the nature of the solvent medium in which they are carried out. Thermal reactions have been by far the more studied, but little progress has been made towards supplying theoretical explanations of the "solvent effect." It may be advantageous, however, before discussing the scanty data on photochemical reactions, to indicate the more important points which emerge from the more accurate work on thermal reactions. These are :—

(1) Attempts to correlate reaction velocity in solution with physical properties of the solvent have met with little success. Amongst the physical properties tested in this connection the dielectric constant is the most prominent, as it is frequently found that reaction rates are greater in solvents with high dielectric constants than in those with small dielectric constants. Many exceptions are, however, known.

(2) While in thermal bimolecular gas reactions every collision between molecules of the right type and for which the combined energies exceed the heat of activation leads to reaction, this would seem not to be the case for reactions in liquid solution (Christiansen, *Z. physikal. Chem.*, **113**, 35, 1924). Very much smaller rates of reaction are here encountered, pointing to deactivating effects of molecules of the solvent at the moment of collision.

(3) In addition to the large deactivating effect always present, there is evidence that a polar solvent may at the same time exert a smaller reverse effect by creating an induced polarity on the reactants with the absorption of energy and consequent lowering of the critical increment of reaction (Norrish and Smith, *J.C.S.*, p. 129, 1928).

Turning now to photochemical reactions, specific effects of solvents are also found for reactions which do not obey the Stark-Einstein Law. (Reactions following the Law of Photochemical Equivalence in presence or absence of solvent are the chlorination of CCl_3Br in CCl_4 and in $SiCl_4$, the bromine-sensitised oxidation of CCl_3Br in CCl_4, and the bromine-sensitised conversion of maleic ester into fumaric ester in CCl_4.) Little work of a systematic character on the influence of solvent medium has, however, been carried out, and, unfortunately, some of the data obtained are of little use for comparative purposes owing to the unsuitable nature of the reactions studied. No general conclusions may legitimately be drawn from these investigations, except possibly that the influence of solvent on photochemical reaction velocity is a composite one. In terms of modern theories, the solvent might modify both the primary and the secondary processes, its effect on the latter being in general of a nature similar to that operating in "dark" reactions. Leaving aside reactions whose primary processes might be highly susceptible to influences exerted by the solvent, one would in general expect solvent effects to be most pronounced in reactions in which secondary processes play a predominant rôle, since in "ideal" light reactions the velocity should be determined only by the rate of absorption of energy. Also, it might be anticipated that, even when secondary processes exert a marked influence on the rate of reaction, the solvent effect should be found on the whole to be smaller in photoreactions than in thermal processes. Regarding the possibility of an influence of the solvent on the primary process, it is, of course, well known from many investigations of absorption spectra in solution that the solvent may (1) shift the position of maximum absorption and (2) increase or decrease the maximum absorption coefficient. Similar effects are also observed in the line absorption of monatomic gases which is influenced by addition of inert gases (cf. the absorption of the 2537 Å line by mercury vapour in presence of foreign gases, studied by Füchtbauer, Joos, and Dinkelacker, *Ann. Physik*, **71**, 204, 1923). While these influences are doubtless due to the mutual action of the electrical fields of neighbouring molecules, practically nothing is known regarding the changes which the electron orbits undergo even in the simplest cases. Thus, it is not known whether, in any given case of absorption of light of a certain frequency, the resultants of the primary process possess unaltered, enhanced, or diminished chemical reactivities consequent on solvent action. A retarding effect of solvation has been inferred in some cases. Thus, Andrich and Le Blanc (*Z. wiss. Phot.*, **15**, 148, 183, 197, 1915) concluded that there exists a connection between the rate of bromination of toluene (by ultra-violet light) in various solvents and the type of absorption spectrum of bromine in these solvents. They found that reaction was rapid in hexane solution but very slow in ethyl acetate. In the first of these solvents the absorption spectrum in the ultra-violet is selective, resembling that of free bromine, while in ethyl acetate the absorption is continuous, the change being due, according to Andrich and Le Blanc, to association of solvent and solute, absorption of the same quantum now yielding a product less capable of reacting with toluene. On the other hand, Scheibe (*Ber.*, **60**, 1406, 1927) draws from absorption data conclusions in a sense opposed to those of Andrich and Le Blanc, though, as they relate to a different reaction, direct comparison is not possible. He finds that the displacements of the maximum of the ultra-violet absorption band of ethyl iodide in various solvents are in the same order as the velocity constants of the thermal reaction between ethyl iodide and triethylamine in these solvents, both variables increasing on passing from hexane to acetonitrile. The shift in the band he regards as a solvation effect, and the increased solvation in acetonitrile compared with that in hexane as making easier the formation of activated molecules of ethyl iodide. It is to be admitted that, at the present state of our knowledge, conclusions of such a kind derived from the absorption spectra of liquids are largely hypothetical, and that the effect of solvent on absorption and its relation to the activation of the primarily formed products are probably complex phenomena not yet capable of satisfactory interpretation.

As stated above, the experimental data for the effect of solvent on photochemical reaction rate are somewhat meagre, and in practically no case have simultaneous measurements of energy absorption and reaction velocity been carried out. Furthermore, some of the reactions are exceedingly complex—they may, for example be associated with after-effects or autosensitisation, or the reactants or resultants may interact with the solvent, etc.—and it is thus difficult to assess in these cases the magnitude of the " true " solvent effect. Reactions of such a type are the oxidation of iodoform studied by Plotnikow (*Z. physikal. Chem.*, **75,** 396, 1905), the bromination of toluene (Bruner and Czarnecki, *Bull. Akad. Sci. Cracow*, p. 516, 1910), and the oxidation of ethyl iodide (Stobbe and Schmitt, *Z. wiss. Phot.*, **20,** 57, 1920). A more straightforward case is the polymerisation of anthracene, investigated by Luther and Weigert (*Z. physikal. Chem.*, **75,** 396, 1911) in a variety of solvents. They found that the rate of reaction was greatest in benzene, and decreased (in the order given) in toluene, xylene, anisole, and phenetole. Consideration of these results and of those obtained by Plotnikow for the oxidation of iodoform in CCl_4, C_6H_6, CS_2, C_2H_5OH, and other solvents led Winther (*Trans. Faraday Soc.*, **21,** 595, 1926) to suspect a connection between reaction velocity and dielectric constant of the medium, increase in dielectric constant being attended by a fall in velocity of the photochemical reaction. This correlation would be in the opposite direction to that which has been presumed to exist in the case of thermal reactions, but it is very doubtful if the supposed connection really exists. Comparison of the data for other reactions certainly fails to substantiate it.

Allmand (*Chem. Soc. Ann. Reports*, p. 351, 1925) has given a summary of recent investigations of photo-reactions whose velocities have been determined in more than one solvent. The cases dealt with include the following. The oxidation (by air) of derivatives of the acid chlorides of benzene sulphonic acid takes place more readily in ether than in chloroform ; in carbon disulphide and in carbon tetrachloride the rate of oxidation is zero (Olivier, *Rec. trav. chim.*, **36,** 117, 1916). According to Lifschitz and Joffe (*Z. physikal. Chem.*, **97,** 426, 1921), the action of ultra-violet light on certain leuco-compounds of the triphenylmethane series is more pronounced when alcohol is employed as a solvent than in ether or benzene. Plotnikow (*Z. wiss. Phot.*, **21,** 117, 1922) finds that the rates of photo-polymerisation of vinyl chloride in different solvents are in the following order : CCl_4 (greatest), C_2H_5OH, CH_3OH, $(C_2H_5)_2O$, $(CH_3)_2CO$, C_6H_6, $C_6H_5CH_3$, and CS_2 (zero rate). According to Meyer and Eckert (*Monatsh.*, **39,** 241, 1918), the photo-oxidation of dihydroanthracene is more rapid in acetic anhydride or in ethyl alcohol than in methyl alcohol ; and von Euler (*Ber.*, **49,** 1366, 1916) obtains greater rates of photo-decomposition of halogenoacetic acids in ether than in benzene. Finally, the photochemical conversion of *N*-chloroacetanilide into *p*-chloroacetanilide takes place more readily in ethyl alcohol than in benzene or glacial acetic acid (Mathews and Williamson, *J. Amer. Chem. Soc.*, **45,** 2574, 1923). While these observations show that the relation—suggested by Winther—between dielectric constant of the solvent and rate of reaction has little applicability, it does not appear that any other general conclusion may be drawn from them. Further work on a few well-chosen reactions is necessary, though probably it will be admitted that these are not easy to find in view of the complications possible with organic solvents and solutes.

INFLUENCE OF TEMPERATURE ON PHOTOCHEMICAL REACTION VELOCITY.

The variation of the velocity of homogeneous *thermal* reactions with temperature is, as a rule, such that an increase of temperature of 10° C. doubles or trebles the velocity, i.e. the temperature coefficient (defined as the ratio of the velocity constants at $(T^\circ + 10^\circ)$ and T°) is most frequently of the order of two to three. It was shown by Arrhenius in 1889 that the relation between velocity constant and temperature is expressible by an equation of the form

$$\log_e k = A - E/RT,$$

in which k is the velocity constant and A and E constants, the latter having the dimensions of energy. This equation he interpreted by assuming the existence of an equilibrium between normal and "active" molecules, only the latter being capable of undergoing chemical reaction. The "active" molecules result from normal ones by an endothermic reaction; the concentration of "active" molecules therefore increases with rise of temperature, and (with small fractional concentrations of "active" molecules) the variation in their concentration with temperature is given by

$$\frac{d \log_e K}{dT} = \frac{E}{RT^2},$$

where K is the equilibrium constant between normal and "active" molecules, i.e.

$$K = \frac{[\text{Active Molecules}]}{[\text{Normal Molecules}]}.$$

E is therefore the heat absorbed in the formation of one mole of the active form and is termed the heat (or energy) of activation. This concept has formed the basis of the intensive work of the past two decades on reaction velocity, though the views of Arrhenius have been slightly modified in attempting to define more precisely what is meant by energy of activation and also to determine the mode of its acquirement by the reacting molecule. It would take us too far afield to attempt anything like an adequate discussion of these points, but we may give a brief summary of certain features of thermal kinetics which are of interest from a photochemical standpoint. Confining our attention to homogeneous reactions in gaseous systems, which are more amenable to theoretical treatment than reactions in liquids, and dealing first with bimolecular reactions, it is found that—with one exception—the velocities of these are well reproduced by the expression

$$k_2 = (\text{collision number}) \times e^{-E/RT} \quad . \quad . \quad . \quad (1)$$

In this equation k_2 is the bimolecular velocity constant, and E is the energy of activation as given by the Arrhenius equation above. For the cases studied (decomposition of HI, N_2O, Cl_2O, CH_3CHO, and combination of H_2 and I_2), E has values between 20,000 and 55,000 cal. The simplest interpretation of this result—there are others—is that the collision itself supplies the energy of activation, i.e. that reaction occurs as a result of practically all collisions between molecules of the right type whose combined energies of translation exceed E/N_0 (N_0 = Avogadro number).* The increase of velocity with temperature is due practically entirely to increase in the value of the term $e^{-E/RT}$, though there is also a small increase in the collision number term (which is proportional to $\sqrt{T}$) with increasing temperature. This latter term is of comparatively greater significance in certain photochemical reactions. The only thermal bimolecular gas reaction hitherto found to occupy an exceptional position is the decomposition of ozone, whose velocity is considerably greater than that predicted by equation (1), and whose heat of activation is greater than that which could be supplied by the translational energy of colliding molecules.

Trimolecular gas reactions (of which three or four are known) are of interest because increase of temperature is found to have very little influence on their velocity, and indeed in one case (the combination of NO and O_2) the velocity *decreases* on raising the temperature. This inversion of the usual effect would seem to be due to a very small energy of activation combined with a diminished probability of occurrence of the necessary ternary collision with increase of temperature. It appears that, owing to increasing velocity of molecular motion, the chance that two " colliding " molecules shall remain within each other's sphere of influence sufficiently long to enable a third molecule to " collide " with the pair becomes the smaller at higher temperatures. In the NO—O_2 reaction, this retarding effect of temperature more than counterbalances the effect of an increased number of collisions for which the necessary energy of activation is available. In photochemical reactions we also find cases of temperature coefficients which are less than unity; they are, however, due to different causes.

It is unimolecular reactions which present the greatest theoretical interest, accompanied, as is known, with difficulties in their interpretation. The present position is somewhat as follows. The Radiation Theory of Chemical Reactivity,* developed by Trautz, Perrin, and W. C. M. Lewis, which has attracted much attention and stimulated much fruitful activity in this field, would appear definitely to have failed to account for the experimental facts. The alternative theories of activation by collision meet with two difficulties, (1) in accounting for the independence of the velocity coefficient of a unimolecular gas reaction on the total pressure, and (2) in showing how the energy of activation can be supplied at a rate sufficient to keep step with the observed rate of transformation of reactants. Christiansen and Kramers (*Z. physikal. Chem.*, **104,** 451, 1923) suggested a "chain" mechanism for unimolecular processes (on somewhat the same lines as "chain" processes in photo-reactions) which formally meets both difficulties. According to them, a molecule of reaction product immediately activates by collision a fresh reactant molecule; the supply of activated molecules is thus maintained, and the velocity constant becomes under certain conditions independent of the pressure. It cannot be said, however, that the "chain" theory of unimolecular reactions has gained general acceptance. It encounters the same difficulty as do "chain" theories involving activated molecules in photo-reactions, the assumption being necessary in both cases that the transfer of energy from activated resultant molecules is highly specific and occurs only upon collision with molecules of reactant. Further, the theory is applicable only to exothermic reactions, yet the best authenticated unimolecular reaction, the decomposition of N_2O_5, appears to be endothermic.

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* For a detailed discussion of the nature of activation in these simple bimolecular reactions, see Hinshelwood (*Kinetics of Chemical Change in Gaseous Systems*. Oxford, Clarendon Press, 1926).

Lindemann (*Trans. Faraday Soc.*, **17,** 598, 1922) suggested that the rate of activation (by collision) is normally much greater than the rate of reaction, and that there exists a time interval between activation and reaction, the activated molecule decomposing only when it attains a certain internal phase of instability. It follows that if the time between collisions is short compared with the average time between activation and decomposition, the condition necessary for the velocity constant to be independent of the pressure is fulfilled. By reducing more and more the pressure of the system, however, a state should eventually be reached in which the rate of activation becomes so small as to be comparable with the rate of reaction; the (fractional) stationary concentration of activated molecules should thereby be lessened and the velocity constant decreased. This postulated diminution in velocity constant at low pressures has not so far been observed in the case of N_2O_5 decomposition (tested down to pressures of 0·002 mm.), but has recently been realised in certain new examples of unimolecular reactions, namely, the decompositions of dimethyl ether, diethyl ether, and propionic aldehyde (Hinshelwood) and the decomposition of azomethane (Ramsperger).† In each of these reactions, the unimolecular constant is independent of the total pressure when this is high; below a certain limiting pressure, however, the constants begin to fall and become less and less the greater the diminution in pressure. A further observation of interest was made by Hinshelwood. In each of the three reactions studied by him, it was found that the velocity constant in mixtures containing hydrogen did not begin to fall on decreasing the pressure below the above-mentioned limiting value, but remained constant. Hydrogen alone of the gases tested exerted this effect; helium and nitrogen, for example, were without action. The remarkably specific nature of this influence of hydrogen has yet to be accounted for.

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* Cf. W. C. M. Lewis, *A System of Physical Chemistry*, Vol. III. (Quantum Theory), p. 223. London, Longmans, 1924.

† The *photochemical* decomposition of azomethane, $CH_3 . N = N . CH_3$ has also been studied by Ramsperger (*J. Amer. Chem. Soc.*, **50,** 123, 1928'

The other difficulty connected with unimolecular reactions consists, as already mentioned, in accounting for the fact that their rates are much greater than the maximum rates of activation possible on the view that only the mutual translational energy of two colliding molecules is transformed into energy of activation of the one. This difficulty is obviated if the assumption be made that the thermal energy associated with the *internal* degrees of freedom of the (usually complex) reacting molecules is also available for activation, and this is the view most favoured at the present time. We shall not here discuss this theory, but refer the reader to the writings of G. N. Lewis and Smith (*J. Amer. Chem. Soc.*, **47,** 1508, 1925), Christiansen (*Proc. Camb. Phil. Soc.*, **23,** 438, 1926), Hinshelwood (*Proc. Roy. Soc.*, **113** A, 230, 1926), Fowler and Rideal (*ibid.*, **113** A, 570, 1927), and O. K. Rice and Ramsperger (*J. Amer. Chem. Soc.*, **49,** 1617, 1927).

Before leaving thermal processes, reference may finally be made to two gaseous reactions which proceed *via* the intermediate formation of atoms. These are the union of H_2 and Br_2 and the formation of phosgene from CO and Cl_2. Both these are somewhat complex reactions, whose mechanisms, however, appear to have been satisfactorily worked out. As we have seen (pp. 465, 575), considerations based on the temperature coefficients and on the correlation of the thermal and photochemical rates of these two reactions have yielded important results in respect of the nature of reactions involving atoms (cf. Bodenstein, *Sitzungsber. Preuss. Akad. Berlin*, p. 104, 1926).

We have seen that in thermal reactions transformation occurs only in certain molecules whose kinetic or internal energies are much greater than the average, and also, as a rule, a definite connection exists between

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using ultra-violet light of wave-length 366 $\mu\mu$. The quantum yield obtained was 2, independent of the pressure between 260 mm. and 1·2 mm. and of the temperature between 20° and 100°. This result is of interest in connection with Christiansen and Kramers' "chain" mechanism of unimolecular processes. It shows that the photo-reaction is definitely not a long chain process, and it is, therefore, unlikely that the thermal reaction with its lower energy of activation can be a chain. On the other hand, Ramsperger considers that the photo-process does form a *short* chain, possessing two links, the activated ethane molecules resulting from the primary decomposition being capable of activating fresh azomethane molecules. A resultant of the ensuing secondary decomposition has, however, insufficient energy to activate a third azomethane molecule, so that the quantum yield does not exceed two.

the action of such "preferred" molecules and the temperature. The number of such thermally-activated molecules is beyond our control; in photochemical reactions, on the other hand, we are able to produce an exactly known number of potentially active molecules which—if monochromatic light be employed—have a known energy of activation. In the simplest photochemical reactions, therefore, in which every activated molecule reacts in a simple stoichiometric manner, we expect to find that with constant illumination the reaction rate should be independent of temperature (except in so far as the absorption of light is subject to variation with temperature). In other cases, unless the influence of secondary processes requiring thermal activation is excessively great, we should anticipate considerably lower temperature coefficients for photo-reactions than for purely thermal processes. These expectations are, in general, confirmed. Thus, the photo-decomposition of HI has the same quantum yield at 20° as at 175° C., and many photo-reactions with temperature coefficients less than 1·05 are known. In general, while in homogeneous thermal reactions temperature coefficients of between 2 and 3 are the rule, the majority of photo-reactions have temperature coefficients less than 1·5,* though there are a few cases in which higher values are obtained. Table LIII gives examples from the numerous data available.

It is to be observed that practically all our data on temperature coefficients relate to ratios of velocity coefficients using light of constant intensity, i.e. possible changes in the absorption capacity of the system with increase of temperature have not been taken into account. The best method of determining the effect of temperature on a photochemical reaction is naturally to find the quantum yield at two (or more) temperatures, measuring each time the amount of light absorbed. This has, however, been done only in a few cases, by Kuhn for the photo-decomposition of ammonia, by Macdonald for the decomposition of N_2O, and (apparently) by Ramsperger for the decomposition of azomethane. The results of Macdonald are of interest in bringing to light a very marked change in the absorption (of N_2O) with temperature. He found that the apparent temperature coefficient of the photo-decomposition of this gas in ultra-violet light, i.e. the ratio of the reaction rates at ($t + 10°$) and $t°$, had the value of 1·24. The absorption, however, increased in the same ratio over an interval of 10°,† so that the quantum efficiency of the reaction is really independent of temperature. It is probable that such a large effect of temperature on absorption is exceptional, and that our data on temperature coefficients may be taken at their face value as applying

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* It was Goldberg (*Z. physikal. Chem.*, 41, 1, 1903) who first drew attention to the low values of the temperature coefficients of photochemical reactions.

† The absorption coefficient (α) increased 1·47 times in 10°, but since reaction rate $= kI(1 - e^{-\alpha cd})$ and the conditions of the experiments were such that the light was moderately strongly absorbed, the "apparent" temperature coefficient was less than 1·47. It is also seen that in cases such as this, in which the absorption varies with the temperature, the observed temperature coefficient will vary with concentration of photolyte.

TABLE LIII.

TEMPERATURE COEFFICIENTS OF PHOTOCHEMICAL REACTIONS.

Reaction.	Light.	Temperature Range.	Temperature Coefficient.	Observer.
Oxidation of quinine by chromic acid	Violet	20°—70°	1·04	Goldberg, 1906.
,, ,, alcohol by $(NH_4)_2Cr_2O_7$	,,	20°—30°	1·0	Plotnikow, 1919.
Polymerisation of vinyl alcohol	Ultra-violet	15°—25°	1·03	Plotnikow, 1922.
$2NH_3 \rightarrow N_2 + 3H_2$	,,	20°—500°	1·05	Kuhn, 1923.
$H_2 + Cl_2 \rightarrow 2HCl$	Violet	25°—100°	1·0—1·1	Porter, Bardwell and Lind, 1926.
$HgCl_2 + FeCl_2 \rightarrow HgCl + FeCl_3$	Ultra-violet	20°—60°	1·04	Winther, 1912.
Decomposition of NaOCl	,,	10°—24°	1·06	Spencer, 1914.
,, ,, $K_3Co(C_2O_4)_3$	Blue-violet	12°—22°	1·06	Vranek, 1917
Anthracene → dianthracene	Ultra-violet	80°—137°	1·0	Weigert and Jäckh, 1927.
Decomposition of $(COOH)_2$ in presence of UO_2SO_4	,,	25°—45°	1·035	Anderson and Robinson, 1925.
$2O_3 \rightarrow 3O_2$ (sensitised by Cl_2)	Blue-violet	16°—25°	1·17	Weigert, 1908
$2HI + O_2 \rightarrow I_2 + 2H_2O$	Red	15°—25°	1·18	Berthoud and Nicolet, 1927.
	Ultra-violet	5°—50°	1·39	Plotnikow, 1907.
$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$	Ultra-violet	10°—30°	1·15	Tian, 1916.
	,,	21°—34°	1·32	Kornfeld, 1921.
$H_2 + Br_2 \rightarrow 2HBr$	White	160°—218°	1·5	Bodenstein & Lütkemeyer, 1924.
Bromination of toluene	,,	1°—33°	1·83	Bruner and Dluska, 1907
,, ,, stilbene	,,	0°—20°	2·1	Berthoud and Beraneck, 1927.
$K_2C_2O_4 + I_2 \rightarrow 2KI + 2CO_2$	Red	25°—40°	3·2	Berthoud and Bellenot, 1924.

with but small errors to quantum efficiencies, but at the same time the possibility of large errors should not be lost sight of (cf. p. 511). Attention may, perhaps, also be drawn to the fact that the temperature coefficients given in the literature for certain reactions may be too high, owing to the occurrence of simultaneous "dark" reactions. Since the temperature coefficients of the latter are invariably higher than those of the corresponding photo-reactions, too great values of the temperature coefficients will be obtained if the "dark" reactions be neglected or their effects only partially allowed for.

In spite of these and other possible sources of error in determining temperature coefficients (or variations of quantum yield with temperature), there can be no doubt that the majority of photo-reactions have temperature coefficients less than 1·5, and usually considerably less. Comparison of the temperature coefficients of the same reaction carried out thermally and photochemically shows that the value for the thermal reaction is always considerably higher than that for the photo-reaction. This holds even when the temperature coefficient of the photo-rate is expectionally high. Thus, the photo-reactions possessing the highest temperature coefficients yet encountered are the reactions of potassium oxalate with iodine and with bromine,* with temperature coefficients of 3·2 and 3·15 respectively; the values for the corresponding thermal reactions are 4·36 and 5·99. Also, reactions with very high values of the thermal temperature coefficient do not necessarily have high temperature coefficients photochemically. Thus, we find that the decomposition of potassium cobaltioxalate in the dark has a coefficient of 4·56, while photochemically it is only 1·06.

The photo-reactions hitherto mentioned all have temperature coefficients equal to or greater than unity; there are, however, a few cases in which increase of temperature is stated to have a retarding effect, i.e. there exist reactions with temperature coefficients less than one. These are the formation of SO_2Cl_2 from SO_2 and Cl_2 (Trautz, *Z. Elektrochem.*, **21,** 329, 1915), the combination of H_2 and Cl_2 catalysed by iodine in blue light at temperatures greater than 20° (Padoa, *Gazzetta*, **51,** (1), 193, 1921), and the union of CO and Cl_2 (Chapman and Gee, *J.C.S.*, **99,** 1726, 1911; Bodenstein, *Sitzungsber. Preuss. Akad. Berlin*, p. 104, 1926). The last of these examples has been discussed (p. 577); the second is briefly considered later (p. 660).

The velocities of "ideal" photochemical reactions should be independent of temperature; actually, it is found that while temperature coefficients are small, they are not—in most cases—exactly unity. The interpretation of this fact is clearly to be sought in the causes which produce greater or smaller rates of reaction than those predicted by the Stark-Einstein relation. Two main lines of so dealing with temperature coefficients may be distinguished, the one a general method based on statistical theory, the other applicable only in special cases (namely to reactions whose mechanisms may be inferred with some degree of certainty) and consisting in the summation of the temperature coefficients of the part-processes. The first of the two methods of procedure has been discussed by Pratolongo (*Gazzetta*, **48,** 121, 1918) and Tolman (*J. Amer. Chem. Soc.*, **45,** 2285, 1923); we shall follow here the treatment adopted by the latter. Tolman deals with two cases: (*a*) a "unimolecular" reaction of the type A + $h\nu \rightarrow$ resultants, and (*b*) a "bimolecular" reaction represented by A + $h\nu$ $\rightarrow$ A*; A* + B $\rightarrow$ resultants. In either case, the chance that a molecule of type A, after absorption of light, becomes activated sufficiently to react depends, in general, not only on the radiation but also on the internal (quantum) state of the molecule immediately before the act of absorption. That is to say that molecules in the lowest quantum state may receive too little energy to bring them into the reactive condition, while molecules in the second and higher quantum states, absorbing the same amount of energy, attain the critical energy level necessary for reaction. The distribution of molecules of A among the different quantum states is given by equations of the type

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* The bromine-sensitised transformation of maleic ester into fumaric ester has a still larger temperature coefficient (see p. 659).

$$N_{\mathrm{A}_i} = N_{\mathrm{A}} \frac{p_i e^{-\epsilon_i/kT}}{\sum_0^\infty p_i e^{-\epsilon_i/kT}} \quad . \quad . \quad . \quad . \quad (1)$$

in which N_{A} is the total number of molecules of A present, N_{A_i} is the number in the i^{th} quantum state, p_i the *a priori* probability that a molecule has of being in this state, ϵ_i the energy associated with the i^{th} quantum state, and the summation $\sum_0^\infty$ is carried out over all possible states. The rate of "unimolecular" reaction taking place under the influence of light of frequency ν and density u_ν may now be calculated. We assume that the reaction is one whose velocity is proportional to the radiation density u_ν and that conditions are such that the rate is also proportional to [A] (i.e. weak absorption of light). We may therefore write

$$-\frac{d[\mathrm{A}]}{dt} = k_\nu u_\nu [\mathrm{A}] \quad . \quad . \quad . \quad . \quad (2)$$

in which k_ν is the specific photochemical reaction rate, the rate at which the reaction would proceed with unit concentration of A and unit energy density of frequency ν. Let $a_{i\nu}$ be the chance in unit time that a molecule in the i^{th} quantum state shall absorb a quantum $h\nu$ from the monochromatic radiation of unit density, and $\beta_{i\nu}$ the chance that the activated molecule so resulting will undergo reaction. Then from (1) the rate of reaction is

$$-\frac{dN_{\mathrm{A}}}{dt} = N_{\mathrm{A}} u_\nu \frac{\sum_0^\infty a_{i\nu}\beta_{i\nu} p_i e^{-\epsilon_i/kT}}{\sum_0^\infty p_i e^{-\epsilon_i/kT}} \quad . \quad . \quad . \quad (3)$$

Comparison of equations (2) and (3) gives for the specific photochemical reaction rate

$$k_\nu = \frac{\sum_0^\infty \alpha_{i\nu}\beta_{i\nu}p_i e^{-\epsilon_i/kT}}{\sum_0^\infty p_i e^{-\epsilon_i/kT}} \quad . \quad . \quad . \quad . \quad (4)$$

Assuming that the coefficients $\alpha_{i\nu}$, $\beta_{i\nu}$, and p_i are all independent of temperature, we obtain from (4)

$$\frac{\delta \ln k_\nu}{\delta T} = \frac{1}{k_\nu} \cdot \frac{\delta k_\nu}{\delta T}$$

$$= \frac{1}{k_\nu} \cdot \frac{\sum_0 \alpha_{i\nu}\beta_{i\nu}p_i e^{-\epsilon_i/kT} \,.\, \epsilon_i/kT^2}{\sum_0^\infty p_i e^{-\epsilon_i/kT}} - \frac{\sum_0^\infty p_i e^{-\epsilon_i/kT} \,.\, \epsilon_i/kT^2}{\sum_0^\infty p_i e^{-\epsilon_i/kT}} \quad . \quad (5)$$

Now the second term on the right-hand side of this equation is clearly the average energy of all the molecules (before activation) divided by kT^2, while examination of the first term reveals that it is the average energy (before activation) of the molecules *which absorb and react*, divided by kT^2. We may therefore write equation (5) in the form

$$\frac{\delta \ln k_\nu}{\delta T} = \frac{\bar{\bar{\epsilon}} - \bar{\epsilon}}{kT^2} \quad . \quad . \quad . \quad . \quad (5a)$$

in which $\bar{\bar{\epsilon}}$ is the average energy (before absorption of light) of the molecules which actually react, and $\bar{\epsilon}$ is the average energy of all the molecules of photolyte. A similar treatment applied to "bimolecular" reactions of the type mentioned gives for these

$$\frac{\delta \ln k_\nu}{\delta T} = \frac{1}{2T} + \frac{\bar{\bar{\epsilon}}_A + \bar{\bar{\epsilon}}_B - \bar{\epsilon}_A - \bar{\epsilon}_B}{kT^2} \quad . \quad . \quad (6)$$

Here $\bar{\bar{\epsilon}}_A$ is the average energy of the molecules of A which enter into reaction, $\bar{\bar{\epsilon}}_B$ the average energy of molecules of B which react, and $\bar{\epsilon}_A$ and $\bar{\epsilon}_B$ are the average energies of molecules of A and B respectively. The equation is similar in form to that for "unimolecular" reactions but contains the additional term $(1/2T)$, which arises from the fact that in "bimolecular" reactions collisions between A and B are necessary and the collision number increases with increasing temperature. The value of this term $(1/2T)$ is based on the assumption (valid at least for gas reactions) that collision number is proportional to $\sqrt{T}$; the correction thereby introduced is negligibly small. It is possible, however, as Tolman points out, that for "bimolecular" reactions in liquids this term may become of significance, owing to rise of temperature causing decreased viscosity, which may also increase the collision number.

To compare equations (5*a*) and (6) with the experimental results (expressed as temperature coefficients), we write $r = \frac{k_{T+10}}{k_T}$, in which the k's are the specific photochemical reaction rates (k_ν) at two temperatures separated by 10°, and we obtain

$$\frac{\delta\, ln\, k_\nu}{\delta T} = \frac{k_{T+10} - k_T}{\frac{10(k_{T+10} + k_T)}{2}} = \frac{r - 1}{5(r + 1)} \quad . \quad . \quad (7)$$

Comparing equation (7) with equation (5a) or (6), and neglecting the term for collision number in (6), it will be seen that for reactions whose temperature coefficients are unity ($r = 1$), $\bar{\bar{\epsilon}} - \bar{\epsilon} = 0$ (or $\bar{\bar{\epsilon}}_A + \bar{\bar{\epsilon}}_B - \bar{\epsilon}_A - \bar{\epsilon}_B = 0$), i.e. the average energies of the molecules which react are the same as the average energies of all the molecules. In other words, molecules in the lowest quantum states have as good a chance of absorbing and reacting as molecules in higher quantum states, and preliminary activation of the molecule is unnecessary for reaction to occur. Also, the existence of a large group of photo-reactions whose temperature coefficients are small (less than 1·08) means that for these $\bar{\bar{\epsilon}}$ is only slightly greater than $\bar{\epsilon}$, i.e. only a small preliminary activation is required. For a reaction with higher temperature coefficient, say 1·40, we find from equations (5a) and (7), taking $T = 300$, that $\bar{\bar{\epsilon}} - \bar{\epsilon} = 6000$ cal. per mole, a not unreasonable value for the difference in energy contents between two successive quantum states of a molecule. It is also possible, as pointed out by Plotnikow (*Lehrbuch der Photochemie*), that for certain reactions in liquids, temperature coefficients higher than 1·1 might be due to the above-mentioned increase in collision number with increasing temperature. The viscosity of water decreases by about 20 per cent. for a 10° rise, and this itself might bring about temperature coefficients in liquids of the order of 1·2.

Finally, Tolman obtains an important result by differentiating equation (5a) or (6) with respect to frequency ν. If this is done, we obtain

$$\frac{\delta}{\delta \nu}\left(\frac{\delta\, ln\, k_\nu}{\delta T}\right) = \frac{1}{kT^2} \cdot \frac{\delta \bar{\bar{\epsilon}}}{\delta \nu} \quad . \quad . \quad . \quad . \quad (8)$$

an expression for the variation of temperature coefficient with frequency of activating light. Now, for reactions in which $\delta\, ln\, k_\nu/\delta T$ is not already zero we may expect to find cases in which $\delta\bar{\bar{\epsilon}}/\delta\nu$ is negative, since $\bar{\bar{\epsilon}}$, the average energy of the molecules which react, might decrease with increase in frequency, owing to the fact that molecules in lower quantum states previously unable to react after absorption might be brought into the reactive condition when the magnitude of the quantum is increased. The theory thus predicts that in reactions with temperature coefficients greater than unity, the temperature coefficient should frequently increase with decreasing frequency. This prediction appears to be confirmed by experiment, though it is not certain that the data are numerous enough or sufficiently reliable to establish that the relation is a general one. Padoa and his collaborators (*Atti. R. Accad. Lincei*, **24**, 97, 828, 1915; **25**, 168, 215, 808, 1916; *Gazzetta*, **46**, 127, 1915 ; **47,** 6, 1916) have determined the variations of the temperature coefficients of a number of photo-reactions with wave-length. Thus, they find for the Eder reaction a temperature coefficient of 1·05 in ultra-violet light and of 1·75 in green light. For the hydrogen-chlorine reaction they give the following temperature coefficients : 1·17 in the long wave ultra-violet, 1·2 in violet light, 1·31 in blue light, and 1·50 in the green. A similar rise in temperature coefficient with increasing wave-length has also been found by Padoa for certain photo-reactions in the solid state, namely, the blackening of silver citrate paper and phototropic changes such as that undergone by salicylidene-β-naphthylamine. Finally, the data on the photochemical decompositions of H_2O_2 and of ozone seem to lead to the same conclusion. In the former, a temperature coefficient of 1·15 was obtained by Tian with short wave ultra-violet light, while Kornfeld found 1·32 with long wave ultra-violet. For the decomposition of ozone, Weigert found a temperature coefficient of 1·14 in ultra-violet light while Griffith and MacWillie obtained 1·44 with red and yellow light. The only exception to the rule so far observed appears to be the photo-oxidation of HI in aqueous solution, which, according to Padoa and Vita (*Gazzetta*, **55,** 87, 1925), has temperature coefficients of 1·20, 1·15, and 1·07 in the blue, the green, and the red respectively.

Turning now to the second method of dealing with temperature coefficients, this is applicable to reactions whose mechanisms have been elucidated, and for which the temperature coefficients of the secondary thermal processes are known or may be inferred. The two best examples of the method are found in the work of Bodenstein and his pupils on the combination of hydrogen and bromine and the union of CO and Cl_2, both of which have already been discussed. The H_2—Br_2 reaction in the light has a temperature coefficient of 1·5, in the dark of 2·0, and Bodenstein showed, on the basis of the very similar mechanisms postulated for both processes, that a knowledge of the temperature coefficient of the one enables us to predict that of the other. This comes about because the velocity of the photo-process depends essentially on the rate of the reaction $Br + H_2 \rightarrow HBr + H$—an endothermic reaction with the temperature coefficient 1·5—while the rate of thermal union of H_2 and Br_2 depends not only on this but also on the stationary concentration of bromine atoms as defined by the equilibrium $Br_2 \rightleftharpoons 2Br$. Knowledge of this equilibrium at various temperatures thus makes possible the calculation of the temperature coefficient of the thermal reaction from that of the photochemical, or *vice versa*. Not only that, but the temperature coefficients of this reaction may be calculated—at least approximately—from thermochemical data alone. In this way, one finds that the reaction $Br + H_2 \rightarrow HBr + H$ is associated with an absorption of 15,000 to 18,000 cal. (depending on the value assumed for the heat of dissociation of H_2) ; now, since the reverse *exothermic* reaction involves an atom (H), it is legitimate to assume that it requires no heat of activation. The value 15,000 to 18,000 cal. is therefore the energy of activation required in the reaction $Br + H_2 \rightarrow HBr + H$, and this corresponds in the temperature range employed in the study of the reaction (160°-218° C.) to a temperature coefficient of the order of 1·5.

The case of the $CO—Cl_2$ reaction (discussed on p. 576) is more doubtful. The retarding effect of temperature here found is explained by Bodenstein in terms of the variation with temperature of the equilibrium between $Cl + Cl_2$ and the somewhat hypothetical Cl_3 molecule. Yet the assumption that this substance is an intermediary in the thermal reaction has yielded a completely satisfactory mechanism for this process, and there appears to be no reason for regarding it otherwise than favourably. In the $CO—Cl_2$ reaction, as in the union of H_2 and Br_2, the data on the temperature coefficients of the thermal and photochemical processes appear to be well correlated by prevailing theories of reaction mechanism.

In a few other reactions, certain inferences in respect of the influence of temperature on the component secondary processes may be drawn, though the solution of the problem is not as complete as in the two reactions just mentioned. Thus, considering the potassium oxalate—iodine reaction, the mechanism suggested by Berthoud and Bellenot is

$$(1)\ I_2 + h\nu \rightarrow 2I\,;\ \ (2)\ I + C_2O_4'' \rightarrow C_2O_4' + I'\,;$$
$$(3)\ I_2 + C_2O_4' \rightarrow 2CO_2 + I' + I\,;\ \ (4)\ I + I \rightarrow I_2.$$

If this mechanism be accepted, the effect of temperature on the reaction velocity is to be found in the temperature coefficients of processes (2), (3), and (4). While an increase in the velocities of (2) and (3) increases the net rate of reaction, acceleration of (4) retards the measured process. One might presume, however, that the velocity of (4) is little influenced by temperature (apart from an increase in collision number), and thus that the observed temperature coefficient is due to the activation required by the reactants in processes (2) and (3). Another effect must, however, be considered, viz. that increase of temperature displaces the equilibrium $KI_3 \rightleftharpoons KI + I_2$ towards the right-hand side, i.e. increases the concentration of I_2. If, therefore, as Berthoud assumes, it is the I_2 molecules alone and not I_3' ions which on absorption yield iodine atoms, this displacement of the Jakowkin equilibrium tends to raise the value of the temperature coefficient. It is probable that influences of both these types, namely (*a*) changes in rates of thermal reactions, and (*b*) changes in the equilibrium conditions of complex formation, electrolytic dissociation, etc., with change of temperature, are not uncommon in photochemical processes and must be taken into account in discussing their temperature coefficients. However this may be, secondary thermal reactions are invariably associated with photo-processes, their influence is usually decisive when large temperature coefficients are in question, and it is at least not unlikely that low temperature coefficients are sometimes the result of the increased velocities of all the secondary reactions mutually cancelling each other.

Turning again to the influence of temperature on the primary stage in photochemical reactions, we have seen how Tolman's theory connects the observed temperature coefficient with the process of activation. In reactions in which a halogen is the absorbing substance, it is of interest—assuming the primary process to be dissociation of the photolyte into atoms—to speculate as to whether or not the efficiency of this process depends on the frequency of the light employed. If dissociation into atoms occurs with light of all frequencies above a certain limiting one, then we should expect the temperature coefficient of the reaction in question to be independent of the wave-length.* Such a case is perhaps afforded by the $K_2C_2O_4$—I_2 reaction, whose temperature coefficient, according to Berthoud and Bellenot, is 3·2 both in red light and in blue light. (On the other hand, Padoa finds that the temperature coefficient of the hydrogen-chlorine reaction increases with increasing wave-length.) The results of Eggert and Borinski and of Wachholtz on the influence of temperature and of wave-length on the quantum yields in the bromine-sensitised reactions of maleic ester are also of significance in this connection. They found that for both reactions (the transformation of maleic ester into fumaric ester and the addition of bromine to maleic ester) the quantum yields were dependent on the wave-length, being about twice as great with blue light ($\lambda = 436\ \mu\mu$) as with green light ($\lambda = 557\ \mu\mu$). The ratio $\gamma_{436\mu\mu}/\gamma_{557\mu\mu}$ was found to be independent of the temperature, i.e. the temperature coefficients of both reactions are independent of the wave-length. The magnitudes of the temperature coefficients and their variation with temperature are, however, exceptional. While in photochemical reactions generally, the temperature coefficient is constant within the studied interval of temperature, and in thermal reactions it decreases with increase of temperature, those of both the maleic ester reactions increase with increasing temperature. According to Wachholtz (*Z. physikal. Chem.*, **125,** 1, 1927), while the quantum yield of the transformation reaction (maleic ester → fumaric ester) increases 1·3 times in passing from 4° to 14°, it is doubled by increasing the temperature from 19° to 23·5°. Similarly, for the addition reaction $\frac{\gamma_{15^\circ}}{\gamma_{4^\circ}} = 1{\cdot}2$ and $\frac{\gamma_{24\cdot5^\circ}}{\gamma_{15^\circ}} = 2$. The temperature coefficients of both reactions thus vary markedly with temperature, and that of the transformation reaction attains extraordinarily high values, being about 4 in the neighbourhood of 20°, and from the form of the γ-T curve it may be inferred that at higher temperatures this reaction has temperature coefficients still greater. The interpretation of these results is doubtful. Wachholtz considers that the increase in quantum yield with increasing frequency is due to a change in the efficiency of the primary process, blue light being twice as effective in dissociating Br_2 as green light. This could well be the case since the convergence limit for Br_2 lies at 511 $\mu\mu$ and the green light employed in this reaction was of wave-length 557 $\mu\mu$, that is, between the convergence limit and the wave-length (630 $\mu\mu$) corresponding to the heat of dissociation of bromine (46,000 cal.). The primary process would thus be activation of Br_2 molecules, and the results indicate that—independent of the temperature—half of these activated molecules subsequently dissociate into atoms. This conclusion is opposed to that reached above for the $K_2C_2O_4$—I_2 reaction. There, we inferred from the fact that the temperature coefficients in blue and in red light were equal, that the primary process possessed equal efficiencies at all wave-lengths in the visible. But the convergence limit of the I_2 band spectrum lies at 499 $\mu\mu$, and hence the primary process with red light is to be regarded as the formation of activated molecules just as in the case of bromine with green light. Further work involving the determination of quantum yields of halogen reactions with varying frequencies is necessary to settle this apparent discrepancy.* Little can be said about the cause of the high temperature coefficients of the maleic ester reactions and of their variation with temperature. They are probably not due to an influence of temperature on the primary process, but to changes in the lengths of the secondary reaction "chains," increase of temperature causing a relatively greater increase in the reactions yielding the final products than in those which permanently destroy bromine atoms (cf. the mechanism on p. 458).

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* Unless, as envisaged by Kuhn (*Z. Physik*, **39**, 77, 1926), the halogen atoms resulting from the primary process are endowed with kinetic energies the greater in amount the larger the quantum supplied, and the possession of this kinetic energy facilitates subsequent reaction.

Finally, brief reference may be made to those photochemical reactions exhibiting temperature coefficients less than unity. In addition to the CO—Cl_2 reaction, the photo-combination of SO_2 and Cl_2 and the union of H_2 and Cl_2 (in presence of iodine) have been reported in this connection. Both are complex processes regarding which little is known. The SO_2—Cl_2 reaction, which appears not to be a long chain process (Bonhoeffer (*Z. Physik*, **13,** 94, 1923) finds γ to be 2 or 3) has according to Trautz (*Z. Elektrochem.*, **21,** 329, 1915) a temperature coefficient as low as 0·88 in ultra-violet light. This may, perhaps, be due to causes similar to those operating in the CO—Cl_2 reaction or possibly to a catalytic effect of water vapour being reduced at the higher temperature. The iodine-catalysed combination of H_2 and Cl_2 was studied by Padoa (*Gazzetta*, **51,** 193, 1921), the experiments being conducted in a Bunsen actinometer containing a solution of iodine in KI. The catalytic effect of iodine (which was present only in small quantity) was found to be greatest in violet light and least in the green. It is not known with certainty whether the iodine acted as a sensitiser, presumably not. In blue and violet light, the velocity of the iodine-catalysed process goes through a maximum at 20°, i.e. the temperature coefficient is less than unity at temperatures above 20°. With green light, however, the temperature coefficients are greater than 1, though apparently less than those of the uncatalysed reaction. The mechanism of the catalysed reaction has been discussed by Padoa (*loc. cit.*) and Thon (*Fortschritte der Chemie*, **18,** Heft 11, 1926). The latter suggests

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* Recent measurements by Jost (*Z. physikal. Chem.*, **134,** 92, 1928) bear on this point. He determined the rate of combination of H_2 and Br_2 at 170°, using light of $\lambda = 436$ $\mu\mu$ (region of continuous absorption by Br_2) and of $\lambda = 546$ $\mu\mu$ (band region), and concluded that both spectral regions were equally effective. The table of results given by him seems, however, to show that the quantum yield in blue light was greater than that in green light.

$$I_2 + Cl_2 + h\nu \rightarrow 2ICl; \quad ICl + H_2 \rightarrow HCl + HI; \quad HI + Cl_2 \rightarrow HCl + ICl, \text{ etc.},$$

and also discusses a possible "atom chain" mechanism which might account for the observed retardation with increase of temperature.

PHOTOCHEMICAL AFTER-EFFECTS.

Certain photochemical reactions are found to continue as thermal processes on removal of the source of illumination, i.e. they are followed by after-effects more or less pronounced. Reactions which exhibit this behaviour are all "catalytic reactions" (exo-energetic processes), which may take place slowly in the dark before illumination, in which event, however, the velocity of reaction is considerably increased both during and after illumination.

The photochemical reactions to be considered in this section include two classes: (*a*) those which continue for an appreciable time after removing the light source, and (*b*) those which continue for a brief time only and in which detection of the after-effect requires special methods. The former are those regarded as showing "true" after-effects, but the latter are of more interest from a theoretical standpoint, though their study is not yet very far advanced. Dealing first with "true" after-effects, many examples of these are known, some of which are striking. The decomposition of H_2O_2 in presence of potassium ferrocyanide studied by Kistiakowsky (*Z. physikal. Chem.*, **35,** 431, 1901) is one of these. In aqueous solution H_2O_2, which is insensitive to visible light, is rapidly decomposed into water and oxygen if subjected to illumination in presence of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. The decomposition follows the unimolecular law and continues, with the same value of the velocity coefficient, after the source of illumination is removed. Quite short exposures to sunlight (one minute) suffice to produce the maximum rate of decomposition. Weigert (*Ann. Physik*, **24,** 261, 1907) showed that reaction occurred equally well if the solution of $K_4Fe(CN)_6$ were separately illuminated and then added to the H_2O_2 in the dark. The most probable explanation of the after-effect is that on illumination of the ferrocyanide solution, a catalyst is formed which provokes the reaction. The catalyst may be of colloidal nature ($Fe(OH)_3$?) or possibly may be $Fe^{\cdots}$ ions, whose catalytic action is promoted by OH' ions. Iron salts are known to catalyse H_2O_2 decomposition, and a considerable amount of attention has been paid to this catalysis (see, for example, Spitalsky and Petin, *Z. physikal. Chem.*, **113**, 161, 1924). It seems likely that the mechanism of the photochemical reaction and its after-effect is simply that of the thermal reaction in presence of iron salts, whatever this may be.

Marked after-effects have been observed and studied by Bruner and Lahocinski (*Bull. Acad. Sci. Cracow*, p. 560, 1910) in the photobromination of toluene. In this case the " dark " reaction also occurs when fresh bromine is added in the dark to toluene which has been pre-illuminated in presence of bromine until the colour of the latter disappears. The reaction which occurs both in the light and in the after-effect is substitution in the side-chain, i.e. formation of benzyl bromide. A solution of bromine in toluene in which the light reaction has proceeded to completion (disappearance of all the bromine) preserves for some time the property of being able to react with fresh bromine in the dark—at least several hours at room temperature, but less at 100°. Bruner showed, however, that the after-effect is bound up with the presence of oxygen and disappears if this gas is eliminated from the system. It is believed that on illumination a catalyst for the reaction is formed—possibly an oxide of bromine—and the fact that the after-effect exhibits an autocatalytic course suggests that the same catalyst is also being formed during this reaction. The catalyst is destroyed by substances such as HBr and I_2 which are oxidised by strong oxidising agents, but not by cooling to the temperature of liquid air. It is also to be noted that bromination of the side chain may occur purely as a dark reaction when dilute solutions of bromine in toluene are employed; the mechanism is probably the same as that of the light reaction in presence of oxygen. The kinetics of the photochemical reaction has been studied by Bruner and Czarnecki (*Bull. Acad. Sci. Cracow*, p. 516, 1910), who found that the presence of oxygen caused non-reproducibility of experimental results. Oxygen acts as an inhibitor to the reaction in the initial stages, but, as it slowly forms a catalyst by reaction with bromine, the rate of bromination of toluene, which at the start is small, increases, and a characteristic—but non-reproducible—autocatalytic course is the result. It was not found possible to avoid this behaviour by attempts to eliminate oxygen completely from the system, but addition of small amounts of iodine, which apparently reacts with oxygen under these conditions, had the desired effect. After-effects in the bromination of toluene, heptane, and hexane have also been observed by Pusch (*Z. Elektrochem*, **24,** 336, 1918), who showed also that the rates of bromination (in the light) were much greater (ten to fifty times) than those predicted on the basis of the Stark-Einstein relation; with hexahydrobenzene (the reaction in this case obeying the photochemical equivalent law) little or no after-effect was found.

Another reaction followed by after-effects is the photo-oxidation of iodoform. Szilard (*Z. wiss. Phot.*, **4,** 127, 1904) found that in presence of oxygen, solutions of iodoform in $CHCl_3$ yielded iodine on illumination, and that the reaction continued in the dark after cutting off the illumination. If a little of this illuminated solution be added to a non-insolated solution, which of itself is stable in the dark, reaction also occurs in the latter. Plotnikow (*Z. physikal. Chem.*, **75,** 385, 1911) showed that the after-effect occurred in certain solvents but not in others. In alcohol, acetone, and carbon bisulphide the reaction ceased on removing the source of light, but continued in the dark with benzene, carbon tetrachloride, and ethyl acetate; in the latter cases the " dark " rate was less than the photochemical rate, but still appreciable. As in other reactions which are characterised by after-effects, the process is a complicated one and the nature of the catalyst is not known. After-effects are also found to occur in the cases of the transformation of *N*-chloroacetanilide into *p*-chloroacetanilide in absolute alcohol or in glacial acetic acid (Mathews and Williamson, *J. Amer. Chem. Soc.*, **45,** 2574, 1923), the oxidations of sodium sulphide, cuprous chloride, and benzaldehyde* (Trautz and Thomas, *Z. wiss. Phot.*, **14,** 352, 1906), and the photo-polymerisation of styrol (Stobbe and Posnjak, *Annalen*, **371,** 283, 1910). Bolin and Linder (*Z. physikal. Chem.*, **93,** 721, 1919) find that the decomposition of Fehling's solution (with formation of Cu_2O) in ultra-violet light is followed by an after-effect; Mukerji and Dhar (*Z. Elektrochem.*, **32,** 501, 1926) failed to observe one in this reaction using sunlight. The last-named workers claim to have found after-effects in the following reactions: tartaric acid and bromine; maleic acid and bromine; potassium oxalate and bromine; chromic acid, oxalic acid, and manganous sulphate; sodium nitrite and iodine; ferrous sulphate and iodine; potassium persulphate and potassium iodide; and others. Apparently all these reactions occur in the dark without pre-illumination; according to Mukerji and Dhar, there is a connection between the velocity of the after-effect and the increase in velocity from the pre-insolated " dark " reaction to the " light " reaction, i.e., the greater the acceleration caused by the light, the greater the observed after-effect. It is probable that in many of these reactions, short-period " after-effects " of the type discussed in the following paragraphs do exist, but the validity of the claims made by Mukerji and Dhar is doubtful owing to the method adopted for the comparison of the " dark " rate, the photochemical rate, and the velocity of the after-effect (cf. *British Chemical Abstracts*, A, p. 366, 1926). Summing up, all the photoreactions which exhibit marked after-effects are complicated processes whose mechanisms have so far not been elucidated. Many of them take place as purely thermal reactions or may be induced to do so by slight changes in the experimental conditions (increase of temperature, addition of catalysts); in some of these reactions catalysts of colloidal nature are probably formed, and in all of them the photochemical after-effect would seem to be due to the production of a relatively stable catalyst which is formed on illumination.

The second type of after-effect—that of short duration—has been studied in but few cases, the chief of which are the hydrogen-chlorine reaction and the reaction between potassium oxalate and iodine. The after-effect is due in such cases to the circumstance that they are chain reactions, the secondary reactions initiated by the true photochemical primary process proceeding after the light is cut off for a very short time, which is, however, measurable by special methods. For the hydrogen-chlorine reaction, the work of Weigert and Kellermann already mentioned (cf. p. 449) shows that, when sensitive gas mixtures are used, the secondary processes last about $\frac{1}{40}$ sec. after cutting off the light. The "after-effect" is consequently of the same order of magnitude. In the case of the potassium oxalate-iodine reaction, investigation of the "after-effect" is made possible by the fact that the velocity of the photo-process is proportional to the *square root* of the light intensity. Using the rotating sector method (Berthoud and Bellenot, *Helv. Chim. Acta*, **7**, 307, 1924; Briers, Chapman, and Walters, *J.C.S.*, p. 562, 1926), the "after-effect" was studied in the following way. Suppose the sum of the angles cut out of the disc by the sectors is $2\pi/n$ and the intensity of the light incident on the disc is I. With the disc rotating so rapidly that the duration of the secondary processes is considerably greater than the interval between successive illuminations, and insolating for a time t, conditions are the same as if we had employed continuous illumination of intensity I/n for the same time t. The amount of material transformed in a given mixture of oxalate and iodine (in aqueous solution) placed behind the disc is then given by $k\,.\left(\frac{I}{n}\right)^{\frac{1}{2}}.\,t = \frac{kI^{\frac{1}{2}}t}{n^{\frac{1}{2}}}$. If, however, the disc be rotated very slowly and the solution insolated for the same time t, the photochemical effect would simply be that produced by a light of intensity I acting for a time t/n, i.e. the smaller value $\frac{kI^{\frac{1}{2}}t}{n}$. It therefore follows that the rate of reaction, which for a given sector angle is independent of the speed of rotation of the disc when this is sufficiently rapid, will begin to diminish at a certain velocity of rotation, and that the limiting reaction velocity at very low rates of rotation will be $1/n^{\frac{1}{2}}$ of that at high speeds. Berthoud and Bellenot have obtained experimental confirmation of the anticipated fall in rate of reaction on diminishing the speed of rotation of the disc below a certain critical velocity. The latter was found—under the conditions of their work—to be such as to make the time between successive illuminations about $\frac{1}{5}$ sec., which time must be comparable with the duration of the "after-effect." The theoretical lower limit for the reaction velocity at very small rates of rotation was not, however, attained.

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* Bäckström (*J. Amer. Chem. Soc.*, **49,** 1460, 1927; *Medd. K. Vetenskapsakad. Nobel-Inst.*, **6,** Nos. 15 and 16, 1927) has confirmed the occurrence of after-effects in this case.

Briers, Chapman, and Walters (*loc. cit.*) discuss the "after-effect" from the standpoint of the mean life of the catalysts (or chain of catalysts) formed on illumination. No assumptions are made regarding the nature of the catalyst* but it is postulated that

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* Berthoud and Bellenot postulate that the catalyst is atomic iodine (cf. p. 452 for the mechanism of reaction suggested by them).

(1) the rate of formation of the catalyst is proportional to the intensity of illumination;
(2) the rate of the *net* reaction is proportional to the concentration of the catalyst; and
(3) the rate of destruction of the catalyst is proportional to the square of the concentration of catalyst.

These assumptions, which naturally are also implicit in the reaction mechanism of Berthoud and Bellenot, lead to the expression

$$\frac{d[\mathrm{A}]}{dt} = k_1 I - k_2[\mathrm{A}]^2$$

for the rate of formation of the catalyst A. Placing $\frac{d[\mathrm{A}]}{dt} = 0$ gives, for the concentration of the catalyst in the steady state on illumination,

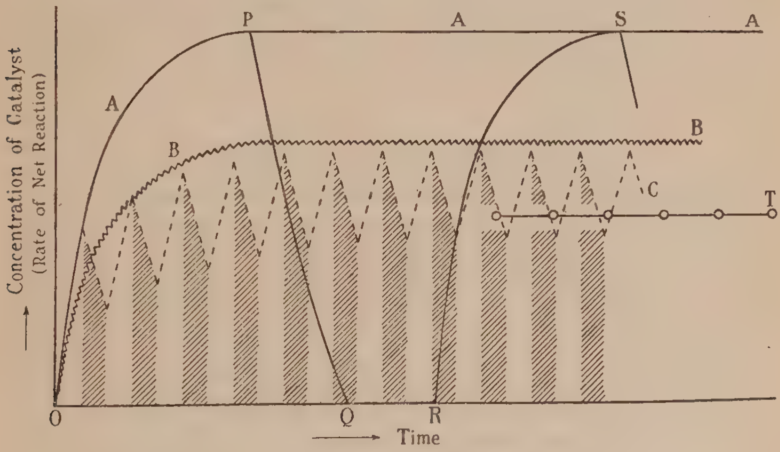

FIG. 52.

$[\mathrm{A}]_s \propto I^{\frac{1}{2}}$. The mean life of the catalyst is given by $\frac{[\mathrm{A}]_s}{k_2[\mathrm{A}]_s^2} = \frac{1}{k_2[\mathrm{A}]_s}$. Chapman and his co-workers carried out experiments similar to those of Berthoud and Bellenot, and, by a mathematical analysis of their results, were able to compute the mean life of the catalyst. Values of 0·03 and 0·12 sec. were obtained in this way, the lower figure with the more intense light. (Theoretically the mean life of the catalyst should be inversely proportional to the square root of the intensity.)

A diagram may possibly be of assistance in illustrating the effects—above mentioned—produced by use of a rotating sector in the investigation of the potassium oxalate-iodine reaction. We consider the case in which the disc has a number of sectors symmetrically spaced, the sum of the sector angles being 180°, so that the duration of a period of illumination is equal to the time during which the light is cut off. Using throughout the same source of light and plotting the concentration of catalyst—or what is proportional to this, the rate of interaction of $K_2C_2O_4$ and I_2—against the time, curve A in Fig. 52 shows the reaction course with *continuous* illumination. Curve B gives the reaction course on inserting the disc and rotating it at high speed. The attainment of the steady state concentration of the catalyst (and of the steady speed of reaction) takes a longer time than in curve A and the value attained is $\frac{1}{\sqrt{2}}$ times, i.e. 70 per cent. of, that of A. Curve C illustrates the reaction course when the disc is rotated at slower speeds, the alternate periods of illumination and of darkness being indicated. The attainment of the steady state takes longer and the velocity reached is less than that in B. Employing very slow rates of rotation of the disc, conditions are approximately represented by OPQRS, in which OP and RS are periods of illumination and PR one of darkness. In this case the concentration of catalyst falls to zero (at Q) some time before the next illumination. The *mean* rate of reaction is represented by the line T and is half that of A.

RETARDATION BY LIGHT.

It is theoretically not impossible that a reaction taking place in the dark should be retarded by insolation, for example, by the formation in the light of an inhibitor of the thermal reaction or by the destruction of a catalyst on illumination. However, there appear to be no cases in which retardation by light has definitely been established. It is true that Trautz and Thomas (*Physikal. Z.*, **7,** 899, 1906; *Z. wiss. Phot.*, **4,** 351, 1906; *Z. Elektrochem.*, **13,** 350, 1907) claimed to have shown that a number of oxidation processes, occurring spontaneously in the dark, are retarded in the light. The reactions studied were the oxidations in aqueous solution by gaseous oxygen of sodium sulphide, sodium sulphite, cuprous chloride, benzaldehyde, and pyrogallol, and it was stated that red light retards some of these processes and accelerates others, a similar claim being made for the effect of violet light. All these are complicated processes, markedly sensitive to inhibitors, and the nature of the work made re-investigation desirable before the conclusions drawn by Trautz and Thomas could be accepted. This has lately been effected by Allmand and Maddison (*J.C.S.*, p. 650, 1927)—at least for the sodium sulphite and cuprous chloride reactions. No retarding effects of light were observed, and it may be concluded that Trautz's results were due to incomplete control of the conditions of experiment, and that they cannot be regarded as evidence of retardation of a thermal reaction by light. Mukerji and Dhar (*Z. Elektrochem.*, **32,** 501, 1926) have also repeated Trautz's experiments and have arrived at the same conclusion as Allmand and Maddison.

SIMULTANEOUS "DARK" AND "LIGHT" REACTIONS.

Reactions frequently encountered in photochemical work are those in which light catalyses processes which occur spontaneously in the dark, so that the observed velocity on illumination is compounded of a "dark" rate and a photo-rate. The separate estimation of the "light" process in such cases may be a problem of some difficulty. It has often been assumed that the true photo-rate may be obtained by subtracting from the velocity measured on illumination the rate determined in the dark under otherwise identical conditions, i.e. it is postulated that the photochemical and thermal processes proceed independently without affecting each other's velocities. Plotnikow (*Lehrbuch der Photochemie*, de Gruyter & Co., Berlin and Leipzig, 1920) has even gone so far as to suggest that this is generally true, and has propounded a so-called "Additivity Law," stating that thermal and photochemical reaction rates are independent. While it is reasonably certain that the "Law" is obeyed in some cases, it is now clear that there are exceptions to it, and that care must be exercised in dealing with the data of all reactions which proceed partly thermally and partly photochemically, when the object is the separate estimation of the photo-rate. It is sometimes possible by suitable alteration in the conditions of experiment (e.g. lowering of temperature, change of concentrations, etc.) to reduce the "dark" rate so that it becomes negligible in comparison with the total rate, and this procedure is to be recommended in order to avoid the necessity of applying what are, at best, somewhat uncertain corrections.

The "Additivity Law" has been discussed by Berthoud (*J. Chim. phys.*, **23,** 251, 1926), who points out that no experimental verification of this "Law" has yet been published, but that there exist several reactions to which it is probably applicable. Thus, in their study of the photo-oxidation of quinine by chromic acid, Luther and Forbes (*J. Amer. Chem. Soc.*, **31,** 770, 1909) obtained results supporting the relation of additivity. They showed that if the "dark" rate of reaction were subtracted from the rates observed on illumination with varying light intensities, the differences were proportional to the energy absorbed by the quinine. The decomposition of ozone in ultra-violet light under the conditions employed by Weigert (*Z. physikal. Chem.*, **80,** 78, 1912) forms another case in which additivity probably obtains, though it is not proven. The "dark" reaction in this investigation was entirely a "wall" reaction, since the velocity of homogeneous thermal deozonisation is inappreciable at temperatures below 50°. As the photo-reaction occurs in the gas phase, it is improbable that the "dark" and "light" reactions affect each other.* Also, in the oxidation of potassium oxalate by bromine, it was considered by Berthoud and Bellenot (*J. Chim. phys.*, **21,** 308, 1924) that the thermal and photo-processes do not influence each other. They found that at temperatures above 10°, when the velocity of the spontaneous thermal reaction becomes appreciable, the velocity in light weakly absorbed by bromine is given by the expression

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* The correction necessary in these experiments could not, however, be determined with accuracy, owing to the erratic nature of the wall-catalysed process. For the methods employed, Weigert's paper should be consulted.

$$-\frac{d[\mathrm{Br_2}]}{dt} = k_1[\mathrm{Br_2}][\mathrm{C_2O_4K_2}] + k_2 I_0^{\frac{1}{2}}[\mathrm{Br_2}]^{\frac{1}{2}}[\mathrm{C_2O_4K_2}],$$

in which the term $k_1\,[\mathrm{Br_2}][\mathrm{C_2O_4K_2}]$ represents the velocity of the "dark" reaction (separately measured), and the succeeding term has the same form as that for the photo-reaction carried out at 0° C., when the "dark" rate may be neglected. On the other hand, Berthoud (*loc. cit.*) criticises the attempt made by Plotnikow (*Z. physikal. Chem.*, **58,** 214, 1907; *ibid.*, **64,** 215, 1908) to establish the additivity relation in the case of the oxidation of aqueous HI by oxygen. Plotnikow measured the rates of oxidation of HI at temperatures of 30°, 40°, and 50°, using a feeble light intensity (I_1) and conditions such that the rates of the "dark" and "light" reactions were of the same order of magnitude; at the same temperatures and with the same concentrations of reactants, the "dark" rates were also measured. He then determined the reaction rates at 10° and 20° using a strong light intensity (I_2), the conditions now being such that the thermal rate was negligible compared with the total rate. Knowing from these last two measurements the temperature coefficient of the "light" reaction and its velocity at 20° with a light intensity I_2, Plotnikow calculated what the velocities of the light reaction should be at 30°, 40°, and 50° with a light intensity I_1, added to these the velocities of the "dark" reactions at these temperatures, and compared the sums with the experimentally determined values. He claimed good agreement between the two and concluded that the "Additivity Law" holds for this reaction. His result, however, depends on the assumption that the velocity of the photo-reaction is proportional to light intensity, a relation which later work has not confirmed. Winther (*Z. physikal. Chem.*, **108,** 236, 1924) has shown that the ratio rate/intensity falls with increasing intensity, while Berthoud and Nicolet (*Helv. Chim. Acta*, **10,** 475, 1927) have found that the reaction velocity is proportional to $\sqrt{\text{intensity}}$. Plotnikow's calculations must thus be regarded as erroneous.

An example of a process for which additivity almost certainly does not hold is the combination of hydrogen and bromine under conditions such that both "dark" and "light" reactions are taking place. As already stated (p. 464), Bodenstein and his co-workers have shown that both processes have essentially the same mechanism, the sole difference being in the mode of formation of bromine atoms, the active agents in the change. In the "dark" reaction, these are formed by spontaneous thermal dissociation of bromine molecules, and an equilibrium defined by the equation $k_1[\mathrm{Br_2}] = k_6[\mathrm{Br}]^2$ or $[\mathrm{Br}] = \sqrt{\frac{k_1}{k_6}\cdot[\mathrm{Br_2}]}$ is set up. The rate of thermal combination of $\mathrm{H_2}$ and $\mathrm{Br_2}$ is given by

$$+\left[\frac{d[\mathrm{HBr}]}{dt}\right]_{dark} = \frac{2k_2[\mathrm{H}_2]\sqrt{\frac{k_1}{k_6}[\mathrm{Br}_2]}}{1 + \frac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br}_2]}} \quad . \quad . \quad (1)$$

(cf. p. 464). In the photo-process, bromine atoms are formed by dissociation of light-activated Br_2 molecules, and we obtain $[\mathrm{Br}] = \sqrt{\frac{A}{k_6}}$, in which A is the number of quanta absorbed per unit of time in unit volume, and the velocity of photo-combination is given by

$$+\left[\frac{d[\mathrm{HBr}]}{dt}\right]_{light} = \frac{2k_2[\mathrm{H}_2]\sqrt{\frac{A}{k_6}}}{1 + \frac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br}_2]}} \quad . \quad . \quad . \quad (2)$$

Under conditions such that the thermal and photo-processes take place together, we find, assuming that the photo-dissociation and the spontaneous dissociation of Br_2 are independent reactions, that

$$k_1[\mathrm{Br}_2] + A = k_6[\mathrm{Br}]^2; \quad [\mathrm{Br}] = \sqrt{\frac{k_1[\mathrm{Br}_2] + A}{k_6}};$$

and

$$+\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2[\mathrm{H}_2]\sqrt{\frac{k_1[\mathrm{Br}_2] + A}{k_6}}}{1 + \frac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br}_2]}} \quad . \quad . \quad . \quad (3)$$

It is clear that the velocity (3) is less than the sum of (1) and (2) and thus that the additivity relation breaks down in this case.

Finally, it is also clear that in those reactions associated with marked after-effects (cf. p. 661) the thermal rate is strongly influenced by the photo-reaction; owing—as one infers—to the formation during illumination of a positive catalyst for the dark reaction, the velocity of the latter during insolation may be much greater than the "normal" dark rate, i.e. the rate before illumination.

Summing up, it can only be said that while additivity of "dark" and "light" reactions probably holds for some of these exo-energetic processes there is always the possibility of disturbing effects, since the majority of them are—photochemically—chain reactions. In the more complex of these reactions, quantitative data for the true "photo" and "dark" rates are difficult if not impossible to obtain; in the others, careful study is necessary before it may be assumed that additivity applies.

APPENDIX.

CHEMICAL EFFECTS OF X-RAYS, α-PARTICLES, AND ELECTRONS.

It is outside the scope of this book to discuss these subjects in any detail, though the chemical effects of X-rays and γ-rays do lie within the true domain of photochemistry. Since, however, the chemical transformations induced by electron collision, by α- and β-rays, and by X- and γ-radiations are frequently of similar nature to those brought about by light, and since also, in some cases, the resemblances between the two seem to extend still deeper, brief reference to certain features of these "radiochemical" processes may here be made. Dealing first with the chemical effects produced by α-particles and comparing them with those brought about by ultra-violet light, we find many reactions common to both modes of activation. However, while the action of light is selective, being dependent on absorption, that of α-rays is universal, practically all systems exposed to their action being altered chemically to some extent. While all types of reaction occur under the influence of α-rays, photolyses appear to be the most frequent, and this doubtless is grounded on the nature of the primary process. Owing to the enormous kinetic energy of α-rays, their primary action is naturally much more violent than that brought about photochemically by insolation with visible or ultra-violet light. While in the latter case only the outer electrons of the absorbing molecule are affected and in most cases there result only activated molecules (one for each quantum absorbed), with α-rays, on the other hand, more deep-seated changes are brought about, complete ionisation occurs, and many molecules—of the order of 10^5—are ionised by a single α-particle.

Considering only reactions in liquid and in gaseous systems which have been studied quantitatively, the feature of such work which is of most interest from a photochemical standpoint lies in the determination of the "radiochemical yield," i.e. the number of molecules transformed per α-particle introduced into the system, or, more correctly, per ion-pair formed. The methods used and results obtained in these investigations have been discussed by Lind (*Chemical Effects of Alpha Particles and Electrons*, 2nd Edition, New York, 1927), who has also been mainly responsible for the development of the technique. In much of the work, a small thin-walled bulb containing radium emanation was mounted centrally in a large bulb containing the reaction mixture, and either static (manometric) or dynamic (analytical) methods were employed for determining the velocity of reaction. Knowing the quantity of radioactive material present, the number of α-particles emitted could be calculated, and knowing the range of the particles and the intensity of the ionisation they produce in air and in other gases, the number (N) of ion-pairs (positive and negative ions) formed in the gas mixture could be estimated with fair precision. Table LIV. summarises some of the results obtained for reactions in gaseous and liquid systems.

Under the column headed M/N is given the number of molecules transformed (or formed) per ion-pair (i.e. the "radiochemical yield"). Many of these reactions have also been studied using ultra-violet or visible light as the activating agency, and the column headed $M/h\nu$ gives the quantum yields obtained. It is clear from the table that there exist distinct similarities between quantum yields and radiochemical yields, though insufficient data make it impossible yet to say how far the parallelism extends. Especially striking is the case of the H_2—Cl_2 reaction, for which not only are both radiochemical and quantum yields exceedingly great under favourable conditions, but also both yields are diminished in the same ratio by inhibitors. As previously pointed out (p. 430), this result implies that while the two reactions have different primary processes, the subsequent secondary processes (the "chain" reactions) are identical. The only other known radiochemical process possessing a high value of M/N is the polymerisation of acetylene ($M/N = 20$). There is, however, no evidence that this is a "chain" reaction; indeed the reverse is true, since the yield is independent of the conditions of experiment.

The remaining reactions of the table all have radiochemical yields not very far removed from unity, and the same applies to the quantum yields (in so far as these have been determined). The figures given in the table for the quantum yields of the reactions between H_2 and O_2 and between H_2 and CO relate to the mercury-sensitised processes. Photochemically, they have been classed as short chain processes; it is of interest that the radiochemical yields are of much the same order of magnitude as the quantum yields. Finally, the other reactions have radiochemical yields between 2·6 and 0·25, and the same is approximately true for the photochemical yields, though the parallelism does not extend beyond the order of magnitude. Lind (*J. Physical Chem.*, **32**, 573, 1926) has briefly discussed these results. In addition to the general similarities above-mentioned, he points out that in one of these processes—the decomposition of ammonia—the parallelism between the α-ray reaction and the photo-reaction extends to the temperature coefficients, which are greater than unity and nearly equal. Thus, $M/h\nu = 0{\cdot}4$ at 20° and 3·3 at 500°, while $M/N = 0{\cdot}8$ at 18° and 2·5 at 350°. Although these similarities exist, they are not specially stressed by Lind (*loc. cit.*) who indicates that there must also be marked differences between photo- and ion-reactions, especially in regard to their mechanisms. In ionisation reactions, it is believed that "cluster-

TABLE LIV.

CHEMICAL REACTIONS INDUCED BY α-RAYS.

Reaction.	*M* in respect of	*M/N.*	*M/hν.*	Observer.
Gaseous : $3O_2 \rightarrow 2O_3$	O_3	0·5	2·0	Lind (1911).
$2NH_3 \rightarrow N_2 + 3H_2$	NH_3	0·8	0·25 0·4	Wourtzel (1919).
Polymerisation of C_2H_2	C_2H_2	20	—	Lind and Bardwell (1926).
$2HCl \rightarrow H_2 + Cl_2$	HCl	0·76	—	Cameron and Ramsay (1908).
$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3	0·25	—	Lind and Bardwell (1928).
$2H_2 + O_2 \rightarrow 2H_2O$	H_2O	4·0	6·6(H_2O_2)	Lind (1919).
$N_2O \rightarrow N_2 + \frac{1}{2}O_2$	N_2O	1·7—2·5	3·9	Wourtzel (1919).
$H_2 + Cl_2 \rightarrow 2HCl$	HCl	5 × 10⁵	2·5 × 10⁵	Porter, Bardwell and Lind (1926).
$H_2 + Br_2 \rightarrow 2HBr$	HBr	0·50	About 2	Lind (1911).
$H_2 + CO \rightarrow H\,.\,CHO$	$H_2 + CO$	3·2	4·8	Lind and Bardwell (1925).
Liquid : $2H_2O \rightarrow 2H_2 + O_2$	H_2O	0·41	—	Usher (1911).
,, ,,	,,	1·0	—	Duane and Scherrer (1913).
$2HBr \rightarrow H_2 + Br_2$	HBr	2·6	2·0	Lind (1911).

ing" plays an important part. The strong electrostatic attraction of the free ion causes neighbouring molecules to cluster on it, and it is suggested that this clustering largely prevents the appearance of chain mechanisms in such reactions.† The view has been advanced, however, that clustering may also occur in photochemical reactions such as the decomposition of N_2O, which has a quantum yield of 4 in short wave ultra-violet light. Here it is perhaps possible that a cluster of four molecules of N_2O is formed after excitation of one of them, and that then the reaction $4N_2O \rightarrow 3N_2 + 2NO_2$ follows.

Energy relationships of a type similar to those found with α-rays seem also probable for chemical reactions initiated by Röntgen or γ-rays, though only one reaction has been quantitatively studied from this standpoint. According to Eggert and Noddack (*Verh. deut. phys. Ges.*, p. 29, 1924), when photographic plates (containing AgBr) are subjected to the action of *X*-rays of wave-length 0·4 Å, about 1000 silver atoms are liberated per quantum absorbed.‡ Nernst and Noddack (*Sitzungsber. Preuss. Akad. Berlin*, p. 110, 1923) have suggested that, with radiation of extremely short wave-length (*X*-rays or γ-rays), the Einstein Law—clearly inapplicable in the form $N = \frac{Q}{h\nu}$ —should be amended to $N = \frac{Q}{h\nu} \cdot \frac{h\nu}{q} = \frac{Q}{q}$. ($N$ = molecules decomposed, Q = energy absorbed, q = energy of dissociation of the absorbing molecule.) In the above case the energy of the quantum employed could (theoretically) decompose about 8000 silver bromide molecules, so that the *energy* efficiency of the process is about $\frac{1}{8}$. Eggert and Noddack (*loc. cit.*) have also obtained yields of corresponding order of magnitude for the action of *α-rays* on photographic plates. Using the α-radiation from niton, they found that each α-particle liberated about 50,000 Ag atoms, while the kinetic energy of the particle was equivalent to the energy of dissociation of 200,000 AgBr molecules. The yield actually obtained is thus of similar order of magnitude to the ionisation yields in gases.

Results of general interest for photochemistry are also those obtained in studies of chemical reactions brought about by electron collision in gaseous systems. This field is a large one and considerable attention is now being paid to it. The processes investigated include reactions under the influence of β-rays, of slow-moving electrons, and of photo-electrons, reactions in the silent discharge, etc. The pheno-

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† In the H_2—Cl_2 reaction, the "chain" process need not begin until electrical neutrality is established. Thus, we might have

$$Cl_2 + (\alpha\text{-ray}) \rightarrow Cl_2^+ + \ominus;\ Cl_2 + \ominus \rightarrow Cl_2^-;$$
$$Cl_2^+ + H_2 \rightarrow H_2Cl_2^+;\ Cl_2^- + H_2 \rightarrow H_2Cl_2^-;$$
$$H_2Cl_2^+ + H_2Cl_2^- \rightarrow 2H_2Cl_2^*;\ 2H_2Cl_2^* + 2Cl_2 \rightarrow 4HCl + 4Cl,$$

followed by the Nernst chain.

‡ The absorption is only about 1 per cent., according to Eggert and Noddack.

mena observed are usually complex, and it would take too long to attempt any discussion of the results obtained. We can, therefore, only refer the reader to the following papers of recent origin, which deal with this subject: $2NH_3 \rightarrow N_2 + 3H_2$ and $3O_2 \rightarrow 2O_3$ in the silent discharge (E. Warburg, *Z. Elektrochem.*, **27,** 141, 1921); theory of chemical reaction in the silent discharge (Elliott, Joshi, and Lunt, *Trans. Faraday Soc.*, **23,** 57, 1927); synthesis of ammonia by electron collision (Buch Andersen, *Z. Physik*, **10,** 54, 1922; Storch and Olson, *J. Amer. Chem. Soc.*, **43,** 1605, 1923; Caress and Rideal, *Proc. Roy. Soc.*, **115**A, 684, 1927; B. Lewis, *J. Amer. Chem. Soc.*, **50,** 27, 1928); the formation of polar compounds under the influence of photoelectrons (W. A. Noyes, Jr., *Trans. Faraday Soc.*, **21,** 569, 1926); and the formation of atomic hydrogen by electronic impact (Hughes and Skellett, *Physical Rev.*, **30,** 11, 1927).

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